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METALLURGICAL ANALYSIS AND ASSAYING

A THREE YEARS' COURSE FOR STUDENTS OF SCHOOLS OF MINES.

BY

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PREFACE

As the title indicates, this Introductory Text-Book has been prepared to meet the requirements of Students of Schools of Mines,—more especially of Colonial Schools of Mines,—the subject-matter being selected to cover a period of three years' laboratory work.

The time necessary to cover the ground, though a somewhat variable quantity, may for a student of average ability be taken as follows:—

(First year.) PART I. Qualitative Analysis and Preparation of Gases, 9 hours per week for 11 weeks and 6 hours per week for 22 weeks, or a total of 231 hours.

(Second year.) PART II. Advanced Qualitative Analysis, 3 hours per week for 33 weeks. Quantitative Analysis, 12 hours per week for 33 weeks, or a total of 495 hours.

(Third year.) PART III. Assaying, 16 hours per week for 33 weeks. Technical Analysis, 8 hours per week for 33 weeks, or a total of 792 hours.

It has been felt by the Authors and others that in no one text-book for the metallurgical student is there laid down a systematic course such as is provided for students of chemical analysis in the works of Newth, Clowes and Coleman and others. The standard works of Beringer and of Furman are of too advanced a nature for the average student, and it is of vital importance that, before working from these text-books, the student should have a thorough training in Qualitative Analysis (Inorganic), simple and complex, and in simple Quantitative Analysis, both Gravimetric and Volumetric. Without such a training the student is not in a position to profit by these works, and can at best but expect to become a mere rule-of-thumb assayer or chemist.

The aim of this work, then, is to fill the existing deficiencies and provide the student with a graded course of work, leading from Simple Qualitative Analysi up to the Technical Quantitative Methods employed by the modern Metallurgical Chemist, and treated of in the works mentioned and the current literature on Chemical and Metallurgical Analysis.

The Authors wish it distinctly understood that they claim no originality of matter, but simply novelty in arrangement, based on experience both in teaching

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and in the routine work of the professional Metallurgical Chemist. Whatever merit the work may possess the Authors consider rests on this claim, and it is their hope that the arrangement herein laid down may be of service both to the Teacher and Student.

Much of the subject-matter is generally regarded as the common property of all chemists, but, where special authorities have been referred to, due acknowledgment, as far as was in the Authors' power, has been made; and if in any case this has been omitted, it has been on account of the difficulty in a far-away State of referring to original sources of information. Any omissions of this nature will be gladly corrected in a future edition.

Though the work herein detailed covers a course of three years' laboratory practice, it is highly advisable that the student extend the course to a fourth year, the details of which may be left to the instructor, or may be selected by the student from the works of Beringer, Furman, and the current literature.

As the time for combined revision of manuscript and proofs has been rather limited, the Authors, in justice to each other, desire to explain that Mr C. Walker is responsible for the sections dealing with Qualitative Analysis and the Preparation and Properties of Gases (pages 1 to 65), and Mr W. A. Macleod for the sections dealing with Quantitative Analysis (pages 65 to 315), Assaying, Technical Analysis, and the illustrations.

W. A. M.
C. W.

CHARTERS TOWERS,
August 1903.

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Prescott and Johnson, Qualitative Chemical Analysis.
Thorpe and Muir, Qualitative Chemical Analysis.
Newth, A Manual of Chemical Analysis, Qualitative and Quantitative.
Caldwell, Chemical Analysis
Valentine and Hodgkinson, Qualitative Analysis.
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Crobaugh, Methods of Chemical Analysis and Foundry Practice.
Poole, Calorific Value of Fuels.
Hillebrand, Bulletin 176, U.S. Geol. Survey.
Smith, Ernest A., Articles on Assaying,—**Chemical News.**
The Analyst, general References.
Journal of American Chemical Society, general References.
New York Engineering and Mining Journal, Articles on the Estimation of Gold and Silver in Copper Products, and general References on Assaying.

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1218. Crucible and lid, porcelain—1 of 14 c.cm. capacity.
1659. Watch-glasses—3 of 5 cm. diam.
1878. Thistle funnel—1 of 30 cm. long (0·3 cm. tube).
444. Retort, glass—1 of 50 c.c. with tubulure and stopper.
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996. Indiarubber tubing—best black, 1 m. of 7 mm. diam., ½ m. of 3 mm. diam.
980. Cork borers—1 set of 3, of brass tube with rod.
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3508. Test-tube brush—1 with sponge end.
1072. Blowpipe—1 Black's japanned tin.
966. Files—1 triangular, 10 cm. long, with handle.
,, 1 round, ,, ,, ,,
1280. Crucible tongs—1 of polished brass, straight, 15 cm.
3523. Test-tube stand.
3517. Test-tube holder—1 wood.
154. Asbestos wire-gauze squares—2 of 15 cm.
801. Filter-paper, cut in circles—2 packets of 100, 11 cm. diam.
3566. Litmus paper—1 packet blue, 1 packet red.
Turmeric paper, 1 packet.
1745. Reagent bottles—3 of 25 c.c. capacity (containing 5% solutions of $PtCl_4$, $AgNO_3$, and 10% sol. $Co(NO_3)_2$.
Glass cloth—1 of 60 cm. × 60 cm.
Duster—1 of 60 cm. × 60 cm.
918. Glass tubing—1 lb. of soft, 0·3 cm. diam.
,, 1 lb. of hard, 0·6 cm. diam.
Pt. wire—15 cm. of 0·3 cm. diam.
Pt. foil—1 piece 3·7 cm. × 2·5 cm. and 1 piece 2 cm. × 2 cm.
201. Bunsen burner—1 cm. tube.
246. Blowpipe jet of brass to fit bunsen.
124. Tripods—2 stout wrought iron, triangular top, 20 cm. high.
1092. Blowpipe charcoal, compressed—1 block 10 × 2·5 × 2·5 cm.
513A. Retort stand and rings—flat iron foot, 43 cm. length of rod.

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PART I.

CHAPTER I.

GLASS WORKING.

Before starting to work at Practical Chemistry it is necessary that the student should have some knowledge of how to cut, bend, draw down, and round off the ends of glass tubing, make closed and bulbed tubes, mend test-tubes, top and bottom, and fit up a decent wash-bottle. In this chapter is included also the graduating of test-tubes and beakers, so that the student from the beginning can work economically with regard to the use of reagents.*

Cutting Glass Tubes. — To cut a glass tube the simplest method is to make a sharp scratch on one side of it with a three-edged file where it is desired to cut, then take the tube in both hands, keep the scratched side from you, and placing the thumbs on either side opposite the scratch, press gently towards you.

If large tubing is to be cut, it is necessary to make a deeper scratch, and sometimes to file to some depth all round the tube.

Where delicate apparatus, such as a test-tube, etc., has to be dealt with, the above method must not be used, but the following:—

Make a scratch with a file and touch it with the end of a very small piece of glass, drawn out and heated at the tip to its melting point. If the heated point is not fine, the fracture is likely to be uneven. To start the crack, it is found best to use glass similar to that being cut. If the crack does not pass quite round the tube, bring the heated piece of glass with which the crack was started to one end of the crack, and slowly move it (nearly touching the glass) in the required direction. The crack will be found to follow the movements of the hot glass.

Bending Glass Tubes.—To bend small tubes and tubes of a moderate size of soft glass, use a fish-tail burner, similar to one used for the purpose of

* The Equivalent System of making up reagents is recommended, and is given in chapter iii. p. 38.

illumination. The flame should be from $1\frac{1}{2}$ to $2\frac{1}{2}$ inches in breadth, so that a fair surface of the tube can be heated and a good bend may result. If a narrower flame is used, less surface of the glass can be heated, and the result is generally a buckling on the concave side.

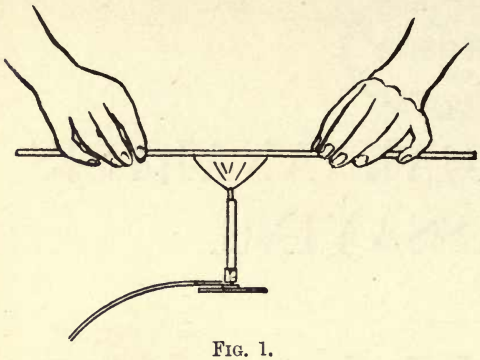

Fig. 1.

The tube to be bent should be held in the position shown in fig. 1, supported by both hands, one on either side of the flame, and should be constantly rotated, so that it may be equally heated on all sides.

When the tube has softened, remove it from the flame and allow it to bend to the angle required by its own weight, slightly relieving the pressure by placing the thumb under the bending end, as shown in fig. 2.

A tube well bent should show no compression or sign of buckling at the bend, and the bore should be of uniform size all through.

When hard glass tubing is required to be bent, the foot blowpipe or a bunsen burner fitted with a fish-tail jet must be used for heating the tubing.

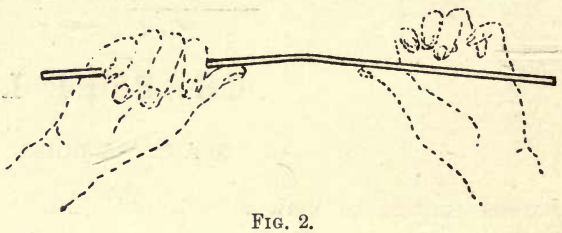

Fig. 2.

Drawing down Glass Tubes. — For the purpose of making a jet for the wash-bottle, a piece of glass tubing the same thickness as is used for the mouthpiece can be drawn down. Take a piece of tubing from 3 to 4 inches in length, hold it in both hands between the thumb and first finger, keeping the thumbs at least $2\frac{1}{2}$ inches apart, and rotate it over a pointed flame. When the glass is sufficiently soft remove it from the flame, still rotating it, and then pull it out suddenly. If the operation is performed successfully, the drawn-down tube will have the appearance shown in fig. 3.

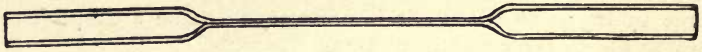

Fig. 3.

A small surface of the glass only is required to be heated, hence a pointed flame is used; and according to the hardness of the glass, so either a small bunsen or a fine blowpipe flame can be used.

Rounding and Bordering the ends of Tubes.—The sharp edges left after cutting glass tubing can be rounded off by holding them in a flame for a few minutes until the glass begins to melt. When the end of the tube is required to be closed by a cork or stopper, its mouth should be expanded a little or bordered. To do this, heat the end of the tube uniformly all round by rotating it in the flame till it softens, then remove it from the flame, at once introduce the charcoal cone, as shown in fig. 4, and rotate it with gentle pressure against the softened glass till the desired effect is produced.

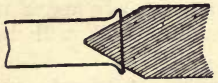

Fig. 4.

Making Closed Tubes.—To make closed tubes it is best to take a piece of hard glass tubing about 7 inches long and $\frac{3}{8}$ inch in diameter, as this will make two closed tubes such as are used in the dry tests in chemistry, without much waste of tubing. Adjust a blowpipe flame so that it will heat a zone of glass about as broad as the diameter of the tube. Hold the tube on each side of the point where it is to be closed, in the same manner as described in fig. 1. Bring the tube gradually into the flame, and heat it with constant rotation till the glass softens. When the glass begins to thicken, gently pull asunder the two ends, taking care not to pull out the softened glass too much, but to allow the sides to fall together, as shown in fig. 5. When this is done, heat the glass at the narrow part till it melts, and pull asunder the two ends. The closed ends should present the appearance shown in fig. 6.

FIG. 5.

If a considerable mass of glass be left at the closed end, it may be removed by heating it to redness, touching it with the pointed end of a cold glass tube, to which it will adhere, and by which it may be pulled away.

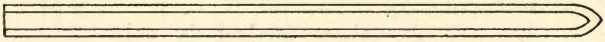

FIG. 6.

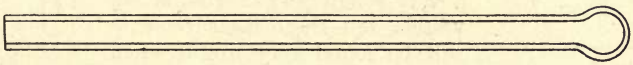

FIG. 7.

Making Bulb Tubes.—To make a bulb tube, make a closed tube first, heat up the closed end in the flame, keeping the tube rotated all the time until the mass of glass becomes thoroughly softened, then remove from the flame, and holding the closed end downwards, blow gently down the tube. Repeat this until the mass of glass at the closed end is worked out to the same thickness as the tube and a bulb is formed similar to the one shown in fig. 7.

Mending Test-tubes.—To mend the tops of test-tubes, proceed exactly as in "Rounding and Bordering the Ends of Tubes," only first cut the tubes off evenly with a piece of hot glass as mentioned in "Cutting Glass Tubing."

To mend the bottoms of test-tubes, cut off evenly as above, and close them with another piece of glass tubing; then gently heat up the closed ends, and proceed as in making bulb tubes, only, instead of blowing, breathe gently into the tubes, as they are made of very thin glass.

Fitting up a Wash-bottle.—Choose a flat-bottomed flask capable of holding from 750 c.c. to 1 litre, also a good cork to fit this flask; in the cork bore two holes parallel to one another, but before boring the holes be sure and soften the cork by wrapping it in a piece of paper and rolling it under the foot. Then take a piece of glass tubing about $\frac{3}{16}$ inch bore and about 9 inches long, and $3\frac{1}{2}$ inches from the end bend it through an angle of from 40° to 45°. Take another piece of tubing of the same bore sufficiently long enough to reach to the bottom of the flask, and pass through the cork $3\frac{1}{2}$ inches, and about 2 inches from one end bend it through an angle of from 135° to 140°. Round the ends of both pieces of tubing and fit them into the cork as shown in fig. 8. Draw down a piece of tubing for a jet and attach it to *b* by a piece of caoutchouc tubing. Fit the cork and tubing into the flask, and a wash-bottle similar in appearance to that shown in fig. 8 will be the result. *b* and *c* together should be equal in length to *a*, and should fall in the same plane.

The glass tubing should fit tightly into the cork, so that when you blow through *a* no air can escape except through *c*.

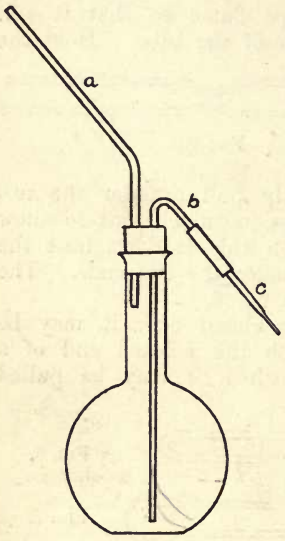

FIG. 8.

Graduating Test-tubes and Beakers.—Take test-tube of about 30 c.c. capacity, clean it thoroughly and dry it; then take a jar of 100 c.c. capacity, graduated in c.c.'s and provided with a spout. Fill the graduated jar up to the 100 c.c. mark with distilled water, keeping the temperature of the water as near as possible to 15° C. Pour out 5 c.c. into the test-tube carefully, and, holding the test-tube in a vertical position, make a small scratch on it with a file at the bottom of the meniscus of the water, then add another 5 c.c. of water and mark the same as before, and so on until 25 c.c. has been measured out. Take a beaker of about 200 c.c. capacity and graduate this in a similar way to the test-tube, only marking it at every 50 c.c. instead of 5 c.c. (fig. 9).

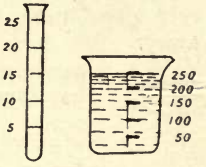

FIG. 9.

The above method is only a very rough way of graduating vessels, but these measurements will be found very useful when different quantities of reagents are required, and quite near enough to prevent students at the beginning of their course using too large quantities, thus avoiding waste.

Blowpipe. Flame test and Borax bead.

A luminous flame is used with the blowpipe, and this can be produced by inserting a piece of brass tubing into an ordinary bunsen burner as shown in fig. 10.

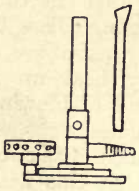

FIG. 10.

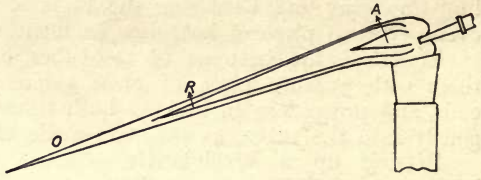

FIG. 11.

The jet of the blowpipe is placed in the flame (see fig. 11), and a steady blast can be maintained by breathing through the nose and keeping the cheeks inflated. The stream of air is not expelled directly from the lungs, but from the mouth by the action of the muscles of the cheeks.

In structure, the blowpipe flame is similar to the ordinary flame, and consists of three distinct cones: the innermost, A, is a cool mixture of air and combustible gas; the middle, R, termed the reducing flame, because there is not sufficient oxygen to cause complete combustion of the gas, and the outermost; O, termed the oxidising flame, where there is a free supply of oxygen from the air, and in which any substance which combines with oxygen at a high temperature is oxidised.

A simple experiment will prove the action of the blowpipe flame at R and O.

In a shallow cavity cut in the surface of a charcoal block (see fig. 12) place a little PbO and allow the point R of the flame to act upon it; in a short time metallic Pb will appear in the cavity, and further along on the charcoal, where the cone O has reached, you will see an incrustation of PbO. Now allow the point O to act upon the reduced Pb and you will notice a film of oxide soon forms on its surface.

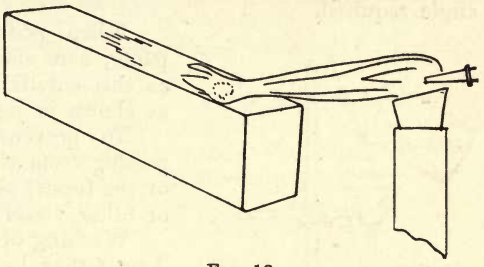

FIG. 12.

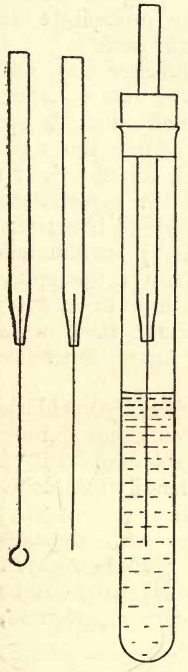

FIG. 13.

In flame reactions the substance to be tested, held either in a loop of Pt wire or on a straight piece of Pt wire, is brought into the lower outer edge of a bunsen flame, when the whole of the outer cone is coloured or rendered luminous by the substance (see fig. 14).

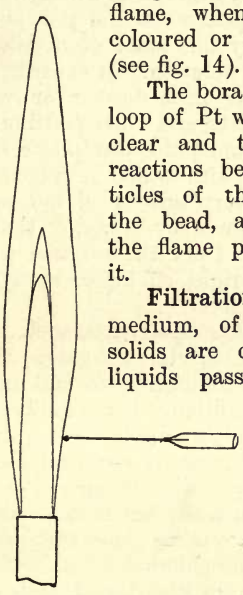

FIG. 14.

The borax bead is made by fusing borax in a loop of Pt wire until the borax when cool is quite clear and transparent. In testing for colour reactions before the blowpipe, very small particles of the substance should be fused into the bead, and care should be taken to form the flame properly before placing the bead in it.

Filtration is the separation, by a porous medium, of solids from liquids, whereby the solids are collected on this medium and the liquids pass through. Porous paper, known as filter paper, and cut in circular pieces of different sizes, is mostly used for this purpose.

These papers are folded as shown in fig. 15 to fit into the glass filter funnels.

The cone of the filter funnel used should always be a little deeper than the filter paper, so that the glass projects slightly above the paper when fitted in.

The filter paper when placed in the funnel should be moistened with distilled water and made to fit closely to the funnel.

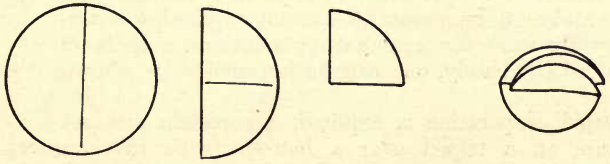

FIG. 15.

If the filter paper, when folded at right angles to the first fold, is too

small to fit closely into the funnel, a second fold should be made at the angle required.

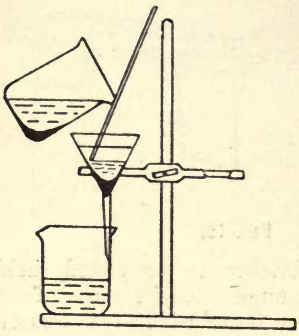

FIG. 16.

When pouring the liquid on to the filter paper, care should be taken to prevent splashing, as this entails loss. Use a glass rod, and pour as shown in fig. 16.

To prevent splashing when the solution is passing from the funnel to the receiver, the stem of the funnel should touch the side of the beaker or other vessel employed as a receiver.

Washing of Precipitates and Residues can be done either by decantation or filtration; in both cases the solution used for this purpose should have no solvent action upon the precipitate or residue. Distilled water is much used.

Decantation is generally the quicker way, and can be used when the precipitate or residue is not in a very fine state of division, and when its sp. gr. is much greater than the wash solution. It consists of adding the wash solution to the precipitate or residue in a beaker or vessel, stirring it up well, allowing the solid matter to settle, and then pouring off the supernatant liquor, and repeating this operation until the precipitate or residue is entirely freed from any trace of the solution with which it was originally surrounded. When the precipitate or residue is very fine or of low sp. gr. it is generally washed on to the filter paper in a funnel by spraying the wash solution from a wash-bottle over it until it is free from the original solution. Each wash solution should be allowed to filter right off before spraying again, otherwise the washing will not be found complete.

Solution is the result of the action of solvents, such as water, hydrochloric acid, etc., on solids, such as metals, salts, etc.; on gases; and on other liquids. What is meant by putting a salt into solution is to add such solvents to it as will convert it totally into a liquid condition. Some solids are readily soluble in their solvents, while others are difficultly soluble and require the application of heat. Solution is accompanied sometimes by chemical changes; this depends upon the nature of the substances employed. If some nitre be placed in water, the result is a solution of potassium nitrate; but if some potassium carbonate be put into hydrochloric acid, effervescence takes place, carbon dioxide is given off, and the result is a solution of potassium chloride.

Evaporation is the conversion from the liquid state to the gaseous or vaporous state, and can be effected either by the application of external heat or without; the latter is termed spontaneous evaporation.

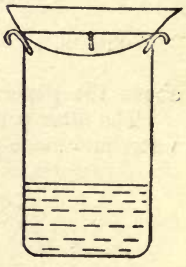

FIG. 17.

The separation of solids from liquids, the concentration of liquids, crystallisation of salts from solution, etc., can be effected by means of evaporation. Where it is necessary to exercise care and high temperatures are not required, a water-bath is generally used for evaporating solutions. If there is not a water-bath handy, one can be improvised as shown in fig. 17.

Where rapid evaporation is required, a porcelain dish set on wire gauze on a tripod over a bunsen (with rose burner) is used, as shown in fig. 18. As the process approaches completion, the flame must be lowered to prevent 'spurting,' which entails loss.

Fusion is the conversion of a substance from the solid to the liquid state by

the application of heat. This must not be confounded with putting a substance into solution. In the case of fusion, after the removal of heat the liquid assumes the solid state again.

Chemical action takes place on fusion sometimes where it does not on solution.

When barium sulphate is fused with about five times its weight of sodium potassium carbonates in a porcelain crucible and the fused mass is treated with water, the solution will be found upon examining to contain sodium and potassium sulphates; and upon treating the residue with hydrochloric acid, it will go into solution with effervescence, and will be found to contain barium carbonate. Barium sulphate is insoluble in hydrochloric acid, so during the fusion chemical action has gone on between the carbonates and the sulphate. (See fig. 19.)

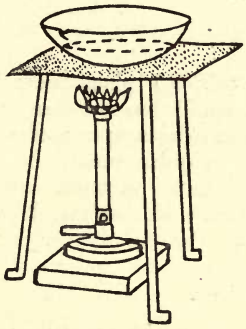

FIG. 18.

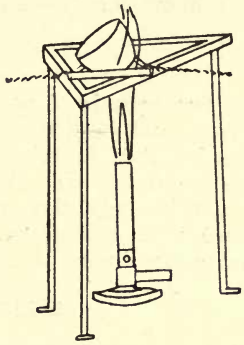

FIG. 19.

Precipitation is the throwing down from solution, by the addition of another substance (usually in solution), of a substance insoluble in the remaining solution. The substance thrown down is called the precipitate. Precipitation is the result of chemical action. If you dissolve a little mercurous nitrate in water and add hydrochloric acid to this solution, you get a precipitate of mercurous chloride thrown down, insoluble in the solution which remains. The hydrochloric acid is called the precipitant. Precipitation may be complete or incomplete. Some precipitates are soluble in excess of the precipitant, hence care must be taken in the addition of the precipitant; on the other hand, if the addition of the precipitant is not sufficient, the result will be incomplete precipitation. Students should always exercise due care with regard to precipitation, and, after filtering, test their solutions to see if it is complete by adding to the filtrate a little more of the precipitant.

Ignition is a term used rather freely in chemistry; it really means the raising of the temperature to that point at which a substance inflames, or in other words, the combustion of a substance; very often in chemistry it is applied to the process of driving off foreign matter from a precipitate by strongly heating. When the student is directed to wash, dry, and ignite a precipitate, the last term is not always used in the sense of decomposing or altering the composition of the precipitate, but simply means ridding it of foreign matter. Heat gently or strongly are terms preferable for use in most cases.

CHAPTER II.

PREPARATION AND PROPERTIES OF GASES.

It is assumed throughout this work that the student has attended or is attending Lectures on Theoretical Chemistry (the non metals, metals, and chemical theory). Without this help he cannot expect any satisfactory progress.

Oxygen.

Take a few crystals of potassium chlorate ($KClO_3$), place them in a clean dry test-tube, and heat them gently over a small bunsen flame; the salt begins to spirt, then fuses. Insert into the test-tube a splint of wood, glowing at the point, but do not allow the wood to quite touch the fused salt. The splint, which only glowed when introduced into the tube, bursts into a bright flame with a slight explosion. Withdraw the splint, blow out the flame, and again insert the glowing end into the tube; the same result follows.

$$KClO_3 \text{ (heated)} = KCl + O_3$$

The above equation explains what takes place in the test-tube; the potassium chlorate breaks up, potassium chloride is formed, and oxygen is evolved. This gas has the property of rekindling a glowing chip.

To prove that the potassium chlorate has undergone a change, take a crystal that has not been heated, dissolve it in distilled water, and add a drop of silver nitrate ($AgNO_3$) solution to it. No change seemingly takes place; the solution remains clear. Now dissolve in distilled water the crystals that have been heated, and add a drop of silver nitrate solution; a white precipitate at once comes down.

$$KCl + AgNO_3 = AgCl + KNO_3$$

To prepare oxygen for experiments, grind about 25 grams of $KClO_3$ in a porcelain mortar, remove to a porcelain dish supported on a tripod over a low bunsen flame, and keep it stirred until the salt is quite dry. Then take about 5 grams of manganese dioxide (MnO_2), dry and mix well with the $KClO_3$. Transfer the mixture to a flask fitted with a delivery tube, and set up your apparatus as shown in fig. 20 *a*. Fill your pneumatic trough with water, then three gas jars; invert them, and stand them on the tray in the pneumatic trough ready to collect the gas (fig. 20 *b* and *c*). Now heat

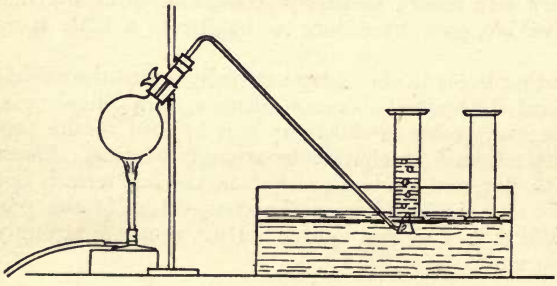

Fig. 20 *a*.

up the mixture in the flask, allow time for the air in the flask to be displaced, and collect the gas by placing the jars one at a time over the hole in the tray under which the delivery tube from the flask passes.

As each jar becomes full of gas slide a greased glass cover under the mouth of it, and stand it aside on the ledge of the trough ready for your experiments.

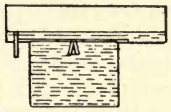

FIG. 20 *b*.

FIG. 20 *c*.

The manganese dioxide is mixed with the potassium chlorate, so that the oxygen may be given off at a lower temperature than it would if the potassium chlorate were heated alone; it does not decompose, but has simply a 'catalytic' action.

Experiment I.—Take a small piece of red phosphorus about the size of a pea, place it in the cup of a deflagrating spoon, set fire to it by bringing it into a gas flame, and plunge it into a jar of the gas (fig. 21). You will observe a brilliant white light is produced, together with dense white fumes. (Do not allow the phosphorus to burn too long in the jar, as the heat may crack the glass.) Remove the deflagrating spoon from the jar, put the cover-glass over its mouth, and allow the jar to cool. When cool, put a little water into the jar and shake it well; the white fumes will disappear, becoming dissolved in the water. Pour into the jar a few drops of blue litmus solution; it turns red, indicating the presence of an acid.

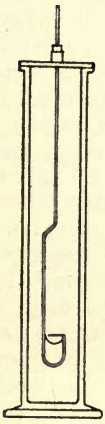

FIG. 21.

The following equations explain the reactions:—

$2P + 5O = P_2O_5$—(phosphorus pentoxide or phosphoric anhydride)
$P_2O_5 + 3H_2O = 2H_3PO_4$—(phosphoric acid)

Experiment II.—Place a small piece of sulphur in the deflagrating spoon, set fire to it, and plunge it into another jar of the gas. You will observe it burns with a pale lavender-blue flame, far brighter than that seen when sulphur burns in air. After the flame goes out, remove the deflagrating spoon from the jar and cover the latter as before. Note the pungent odour of the substance formed, also the apparent absence of anything in the jar; the product of combustion being an invisible gas. Add a little water, shake the jar, and pour in a few drops of blue litmus solution; an acid is again indicated.

The following reactions take place:—

$S + 2O = SO_2$—(S. dioxide or sulphurous anhydride)
$SO_2 + H_2O = H_2SO_3$—(sulphurous acid)

Experiment III.—Place a piece of charcoal in the deflagrating spoon, set fire to it, and plunge it into another jar of the gas. You will observe a comparatively feeble light is produced. Allow the charcoal to burn as long as it will, then remove the spoon and plunge a lighted taper into the jar; it immediately goes out. Now pour in some lime-water and shake the jar; the lime-water becomes turbid, which is due to the action of the gas in the jar.

The following reactions take place:—

$C + 2O = CO_2$—(C. dioxide or carbonic anhydride)
$CO_2 + Ca(OH)_2 = CaCO_3 + H_2O$
(Lime-water) (Turbidity or ppt.)

Hydrogen.

Take one or two grams of zinc, put them in a test-tube, and add a few drops of dilute sulphuric acid; an effervescence takes place, and bubbles of gas rise through the liquid. Put a lighted taper into the test-tube; a slight explosion takes place, and you see a momentary flash.

The following equation explains the reaction that takes place:—

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

To prepare hydrogen for experiments, take a flat-bottomed flask of about 300 c.c. capacity and fit it up with a thistle funnel and delivery tube as shown in fig. 22. Slide carefully into the flask about 30 grams of granulated zinc, inclining the flask to one side while so doing to prevent the zinc from striking heavily on the bottom of the flask, and perhaps cracking it; fit the tube and funnel into the flask, and pour through the funnel sufficient water to just cover the zinc. Fix the flask now on a retort stand with the delivery tube dipping into the pneumatic trough, as in the preparation of oxygen, and get two gas jars ready as before. Add, little by little, dilute sulphuric acid through the funnel, just sufficient to keep up a steady effervescence. Allow time for the air to be displaced in the flask, then collect some of the gas in a test-tube; when full place the thumb under the mouth of the test-tube while under the water and remove it from the trough. Keep the test-tube mouth downwards, remove the thumb and apply a light; if an explosion takes place, the gas is still mixed with air; so repeat the experiment until no explosion takes place, then the gas is ready to collect in the jars. Collect two jars full of the gas, and use cover-glasses as before.

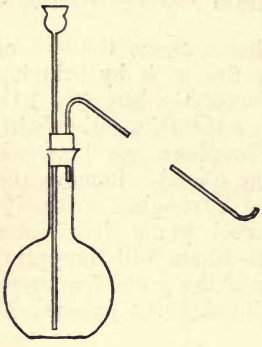

Fig. 22.

Experiment I.—Take a jar of the gas from the trough, and, holding it mouth downwards, remove the cover-glass and apply a light to the mouth of the jar; the gas takes fire and burns with a non-luminous flame; pass the taper further up into the jar and it is extinguished. You will observe that under ordinary circumstances hydrogen is inflammable, but does not support combustion like oxygen.

Experiment II.—Take the other jar of the gas from the trough, keep it inverted in the right hand, while in the left you hold, also mouth downwards, a jar containing air only; pour upwards, as it were, the hydrogen gas into the jar containing the air (see fig. 23), in a few moments all the hydrogen will have passed into the upper jar. Set the jar from which you have poured the gas mouth downwards in the trough and bring a lighted taper to the mouth of the other jar, still keeping it inverted; a slight explosion follows, and then you see the pale non-luminous flame of burning hydrogen. Now take the jar from the trough and apply a light to its mouth; no similar result follows, showing that all the hydrogen has been poured out. This experiment proves the lightness of hydrogen gas.

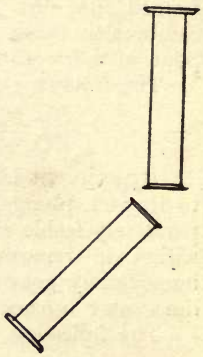

Fig. 23.

Filter the liquid remaining in the flask containing the zinc and sulphuric acid, and evaporate it down to about one-third its bulk in a porcelain basin, then set it aside to cool; white crystals of zinc sulphate will be found to separate out.

The relativity of the terms 'combustion' and 'supporter of combustion' may be shown with gases other than pure oxygen and hydrogen. Air, for instance, may be made to burn in an atmosphere of coal gas. Take an ordinary lamp cylinder and fit it with a cork and glass tubes as shown in fig. 24. Attach *a* to a gas jet and send a current of coal gas into the cylinder; allow time for the cylinder to be completely filled with coal gas, then pass a lighted taper up the open wide tube *b*; a bluish flame is formed, and will continue to burn as long as the current of coal gas is kept passing through the cylinder.

FIG. 24.

In this experiment you see that a gas which, under ordinary circumstances, is combustible, can apparently be converted into a supporter of combustion.

Nitrogen.

Nitrogen exists in the air, mixed principally with oxygen, so the simplest way to prepare it is to take away the oxygen from the air. Fill the pneumatic trough as before with water, and on the tray stand a bell jar, under which float a small porcelain dish containing a little amorphous phosphorus, as shown in fig. 25. Ignite the phosphorus with a red-hot wire; white fumes (P_2O_5) will be seen in the jar, but after a time will become dissolved in the water, and the water will gradually rise in the jar. When the combustion is over and the jar is cool, fill two gas jars with water, place them inverted in the trough, and decant the gas from the bell jar into them, keeping their mouths under the water in the trough.

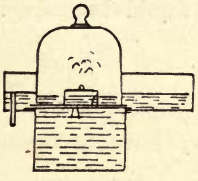
FIG. 25.

Experiment I.—Pass a lighted taper into one of the jars; the flame is extinguished and the gas does not take fire, showing that nitrogen is neither combustible nor a supporter of combustion.

Experiment II.—Into the other jar pour a little clear lime-water, close its mouth with a greased cover-glass and shake briskly; the lime-water is not rendered turbid. This test distinguishes nitrogen from carbon dioxide.

Nitric Acid.

Take a glass-stoppered retort with a capacity of about 250 c.c. and a long beak; clean and dry it. Weigh out 25 to 30 grams of potassium nitrate and transfer it to the retort through either a glass funnel or an improvised paper funnel, taking care that none of the salt adheres to the neck of the retort. Fix up your retort and receiver as shown in fig. 26; calculate how much sulphuric acid will be required according to the following equation:

$$\underbrace{KNO_3}_{39+14+48} + \underbrace{H_2SO_4}_{2+32+64} = \underbrace{HNO_3}_{1+14+48} + \underbrace{KHSO_4}_{39+1+32+64}$$

$$\underbrace{\text{101 parts}} + \underbrace{\text{98 parts}} = \underbrace{\text{63 parts}} + \underbrace{\text{136 parts}}$$

to decompose the potassium nitrate, add it to the contents of the retort and replace the stopper. Gently heat the retort; after a short time you will observe brown fumes rising and drops of liquid forming on the sides of the beak, and running slowly down into the receiver. Keep the receiver cool by allowing water to drop on it as shown in fig. 26.

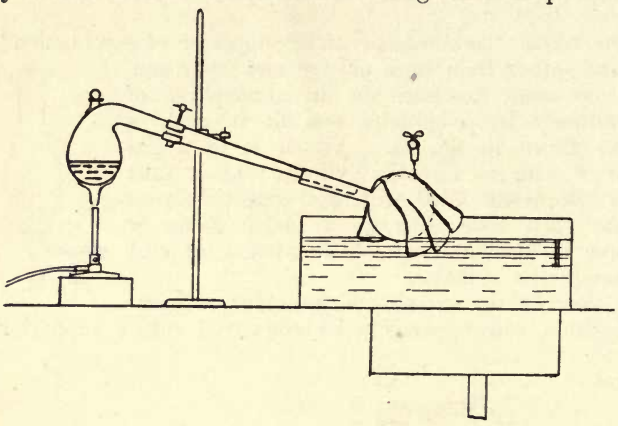

FIG. 26.

The liquid in the receiver, as it accumulates, will be seen to be brownish yellow, heavy, and fuming when exposed to the air. This is concentrated nitric acid.

Experiment I. — Pour a drop or two of this acid into a test-tube, add a little water, then a small strip of copper foil; a violent action follows, a dark reddish-brown gas is given off, and the liquid becomes a greenish colour.

$$8HNO_3 + 3Cu = 2NO + 3Cu(NO_3) + 4H_2O$$
$$2NO + O_2 = 2NO_2 \text{ (reddish-brown gas)}$$

The NO is a colourless gas, as will be seen later on; but coming in contact with the air, it takes up oxygen and forms NO_2.

This is one test for nitric acid.

Experiment II.—Dissolve a few crystals of ferrous sulphate in a little cold water in a test-tube. Into the test-tube used in Exp. I. pour a few drops of nitric acid to cause a fresh evolution of gas. Hold the two test-tubes so that the ruddy fumes may fall into that containing the ferrous sulphate solution, as shown in fig. 27; the clear solution will become rapidly darkened in colour, until it is nearly black. This darkening effect of the oxides of nitrogen, when brought into contact with ferrous sulphate solution in the cold, is another and most delicate test for nitric acid. If you boil the dark solution the colour will be almost all discharged, hence the reason for using a cold solution of ferrous sulphate.

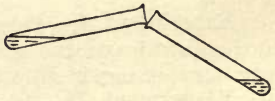

FIG. 27.

Experiment III.—Dissolve a little nitre in water in a test-tube, then add a few crystals of ferrous sulphate; shake the tube until all is dissolved and incline it to one side; pour carefully down the side of the tube a few drops of strong sulphuric acid, so that the heavy liquid may sink to the bottom and there form a separate layer. At the junction of the two layers a dark-brown-coloured ring will be seen, which proves the pressure of nitric acid. The dark-coloured ring is of the same nature as the dark solution of the previous experiment.

$$2KNO_3 + H_2SO_4 = 2HNO_3 + K_2SO_4$$
$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 2NO + 3Fe_2(SO_4)_3 + 4H_2O$$

The above equations show the reactions which take place in the test-tube.

The sulphuric acid acts upon the nitre, forming nitric acid and potassium sulphate; part of the ferrous sulphate is acted upon by the nitric acid, forming ferric sulphate and lower oxides of nitrogen; the latter dissolve in the excess of ferrous sulphate, and give the dark brownish-black colour.

In this experiment care must be taken to keep the solution cool.

Nitrogen Monoxide. (Nitrous Oxide.)

This gas can be prepared from ammonium nitrate, which can be made by neutralising dilute nitric acid with ammonium hydrate. Take some of the nitric acid left over from the last experiments, dilute it with a little water, put it in a porcelain basin, and add ammonium hydrate to it, keeping it stirred with a glass rod until a drop taken on the rod ceases to redden blue litmus paper. Set the basin over a low bunsen flame and evaporate down slowly, adding from time to time a few drops of ammonium hydrate to keep the solution alkaline, until the liquid becomes slightly viscid and shows no signs of ebullition. Set the basin aside and allow to cool.

$$NH_4HO + HNO_3 = NH_4NO_3 + H_2O$$

To prepare the gas for experiments, fix up your apparatus in a way similar to that for the preparation of oxygen. Take about 10 grams of ammonium nitrate and place carefully in the bottom of your flask. Fill your pneumatic trough with warm water instead of cold, as N_2O is soluble in cold water, and set up four gas jars in the trough as before.

Heat the flask gently until the salt fuses, then gradually increase the heat until the fused ammonium nitrate begins to decompose with effervescence and bubbles of gas pass up rapidly through the water in the trough. Allow time for the air in the flask to be displaced, then begin to collect the gas. In heating the flask do not allow the temperature to get too high; if many white fumes arise in the flask, moderate the heat, and when you have collected sufficient gas, remove the cork and delivery tube from the flask to prevent the water rushing up the tube and cracking your flask.

$$NH_4NO_3(\text{heated}) = N_2O + 2H_2O$$

Experiment I.—Take one of the jars of gas from the trough and plunge a lighted taper into it; the flame burns brighter than in air, but the gas itself does not take fire.

Experiment II.—Place a piece of amorphous phosphorus in a deflagrating spoon, ignite it, and plunge it into another jar of the gas; the phosphorus burns almost as brilliantly as in oxygen.

$$5N_2O + P_2 = P_2O_5 + 5N_2$$

After the fumes of P_2O_5 have subsided you can test the remaining gas in the jar for nitrogen by plunging a lighted taper into it.

Experiment III.—Place a small piece of sulphur on the deflagrating spoon, just light it and plunge it into another jar of the gas; the flame is extinguished, the temperature of the burning sulphur not being high enough to break up the gas. Heat up the sulphur now considerably above its melting point and plunge it into the same jar of gas; it burns brilliantly.

$$2N_2O + S = SO_2 + 2N_2$$

Experiment IV.—Pour a little cold water into the remaining jar of the gas, close the mouth with the hand and shake briskly; invert the jar, still keeping the hand over the mouth, and bring it beneath some cold water in another trough;

withdraw the hand and you will see the water rise in the jar; repeat the shaking, and again bring the jar under cold water, and you will see the water rise still more; this shows the solubility of nitrogen monoxide in cold water.

Nitrogen Dioxide. (Nitric Oxide).

Weigh out about 30 grams of copper shavings, put them into a flask fitted with a thistle funnel and delivery tube, and fix up your apparatus in a similar way to that for the preparation of hydrogen. Mix about 60 c.c. of strong nitric acid with about the same quantity of water and pour carefully down the funnel; red vapours will almost immediately fill the flask, but will disappear after the air has been displaced in the flask.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$$

Collect four jars of the gas.

Experiment I.—Plunge a lighted taper into a jar of the gas; the taper goes out and the gas does not take fire, but reddish-brown fumes appear in the jar.

Experiment II.—Place a small piece of amorphous phosphorus in the deflagrating spoon, light it and plunge it immediately into a jar of the gas; the flame is extinguished. Again light the phosphorus by holding it for a few moments in the bunsen flame, and when it is burning briskly plunge it into the jar; the phosphorus burns with increased brilliancy.

$$5NO + P_2 = P_2O_5 + 5N$$

Experiment III.—Plunge a piece of brightly burning sulphur into another jar of the gas; it is extinguished.

Nitric oxide takes a higher temperature to break it up than nitrous oxide.

Experiment IV.—Prepare a jar full of oxygen; decant about one-fourth of the nitric oxide in the remaining jar into another gas jar by means of the trough, and very slowly pass up into this a little oxygen (fig. 28). As the oxygen comes in contact with the nitric oxide, reddish-brown fumes are produced. After adding a small quantity of oxygen, shake the jar containing the mixed gases, keeping its mouth under water to prevent air from getting in; the water will rise, showing the gas is soluble. Continue the addition of oxygen, shaking the jar at intervals; after a time the jar will become entirely filled with water.

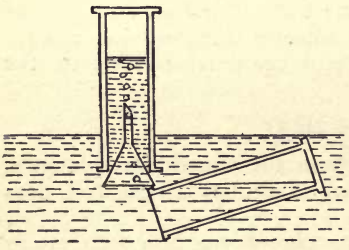

Fig. 28.

$$2NO + O_2 = 2NO_2$$

The NO_2 gas is readily soluble in water. Filter the liquid remaining in the flask and transfer to a porcelain basin, then evaporate it down to about one-third of its bulk and allow the crystals of copper nitrate to crystallise out. These crystals will be of a bluish colour.

Ammonia.

This gas is so soluble in water that it cannot be collected as before over water in the pneumatic trough, and as it is lighter than air, fix up your apparatus as shown in fig. 29 and collect it by upward displacement.

Mix a little ammonium chloride with an equal amount of quicklime and

put it in a test-tube and heat; you will smell ammonia coming off strongly. Repeat the experiment, only using sodium hydrate instead of quicklime; the same result follows. Moisten a piece of red litmus paper reddened by holding it over a little strong hydrochloric acid, and then hold it over the test-tube; it is turned blue.

Weigh out about 10 to 15 grams of ammonium chloride, powder it, and mix it with about an equal weight of powdered quicklime; transfer the mixture to your flask, and then cover the mixture with a little more quicklime in the flask; fix in your cork and tubes as shown in fig. 29. Gently heat the flask; the ammonia gas soon comes off and passes through the second flask, containing a strong solution of ammonium hydrate, into the inverted jar. To tell when the jar is full, moisten a piece of turmeric paper and bring it near the mouth of the jar; if it turns brown it is full; place a cover over the mouth of the jar, and place another over the delivery tube. Collect three jars of the gas.

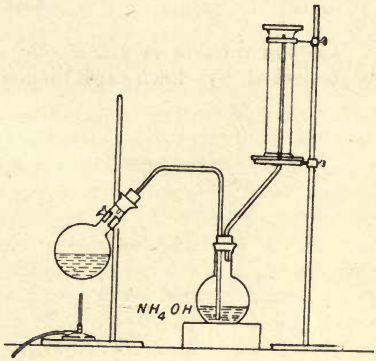

FIG. 29.

$$CaO + 2NH_4Cl = CaCl_2 + H_2O + 2NH_3$$

Experiment I.—Take a jar of the gas, invert it and bring a lighted taper into its mouth; a momentary flash of greenish-coloured flame is noticed near the taper, which is then extinguished.

Experiment II.—Pass your delivery tube up through a cork fitted into a large piece of glass tubing as shown in fig. 30. Also pass just through the cork a tube attached to an oxygen receiver. Start a current of oxygen through the tube, then a current of ammonia gas; bring a light to top of the delivery tube of the ammonia gas, and you will find it will burn with a peculiar greenish-yellow flame.

Experiment III.—Pour 30 or 40 c.c. of strong ammonium hydrate into a small flat-bottomed flask; make a platinum spiral by winding a piece of platinum wire round a piece of small glass tubing, attach it to a small piece of tubing, then heat the spiral in a bunsen flame and plunge it into the flask containing the strong ammonium hydrate to within a centimetre or so of the solution; the spiral will continue to glow and the flask will become gradually filled with white fumes. The heated platinum causes the oxygen of the air to combine with the ammonia, forming nitrous acid (HNO_2), which in turn acts upon the excess of ammonia and forms ammonium nitrite (NH_4NO_2), the white fumes you see in the flask.

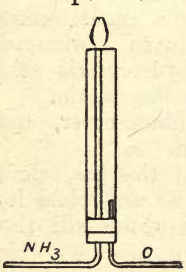

FIG. 30.

Experiment IV.—Put in a flask a few drops of concentrated hydrochloric acid and warm, then bring a jar of the gas inverted over the neck of the flask; dense white fumes immediately appear in the jar.

$$HCl + NH_3 = NH_4Cl$$

Experiment V.—Take the remaining jar of the gas and bring it mouth downwards over the hole of the tray in a pneumatic trough filled with water;

remove the cover-glass and you will see the water rising quickly in the jar, showing the solubility of ammonia gas in water.

$$NH_3 + H_2O = NH_4OH$$

Carbon Dioxide.

Carbon dioxide is about one and a half times heavier than air, so it can be collected by downward displacement. Fit up a flat-bottomed flask with a thistle funnel and delivery tube, and set up your apparatus as shown in fig. 31.

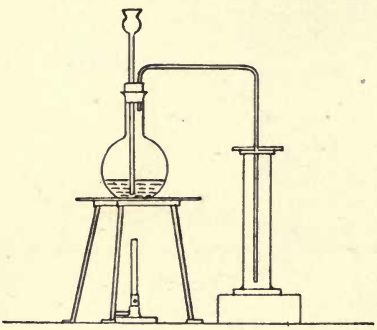

Fig. 31.

Weigh out about 25 to 30 grams of marble, broken into small pieces, and transfer carefully to the flask; then pour a little water into the flask, and fit in the thistle funnel and delivery tube. Pour down the thistle funnel some strong hydrochloric acid; a brisk effervescence follows, and the gas is evolved.

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

Collect three jars of the gas. To test when the jars are full, apply a lighted taper to the mouth of each jar; if it is extinguished, you will know the jar is full.

Experiment I.—Pour a little clear lime-water into a small beaker, dip the end of the delivery tube into this liquid, and allow the carbon dioxide to bubble through it; the clear solution becomes turbid. Continue to pass the gas, and the turbidity disappears after a time. Remove the beaker and boil the clear solution; the turbidity soon appears again.

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

$$CaCO_3 + H_2O + CO_2 \gtrless CaH_2(CO_3)_2$$

Experiment II.—Pour a little blue litmus solution into a small beaker and pass the carbon dioxide gas through it; the solution turns a wine-red colour, differing from the red produced by the action of hydrochloric acid on litmus solution. Boil the wine-red liquid and it becomes blue again.

Experiment III.—Take a jar of the gas, remove the glass cover, and pour the gas on to a lighted taper; the taper soon goes out.

Experiment IV.—Pour a little water into another jar of the gas, close the mouth of it with the hand and shake well; invert the jar and place its mouth under water in a trough; remove the hand and the water will rise in the jar, showing the solubility of the gas.

Experiment V.—Take the remaining jar of the gas and pour a little sodium or potassium hydrate solution into it; close its mouth with the hand and shake well, then invert it and bring its mouth under water and remove the hand; the water will rush into the jar, showing that the gas has been absorbed by the solution of sodium or potassium hydrate.

$$2KOH + CO_2 = K_2CO_3 + H_2O$$

Filter the liquid remaining in the flask, transfer to a porcelain dish and evaporate to dryness, stirring it from time to time to prevent the calcium chloride from sticking to the dish.

Carbon Monoxide

Take a few crystals of oxalic acid and put them into a dry test-tube, then add a few drops of strong sulphuric acid to them and heat gently over a bunsen flame; an effervescence takes place and a gas is given off, which upon applying a lighted taper to the mouth of the tube will be found to burn with a pale lavender-blue flame; the flame will pass down the tube and then go out. Now fix a cork and delivery tube into the test-tube, and pass the delivery tube into another test-tube containing a little limewater; warm up the first test-tube again, and let the gas bubble through the limewater; this soon becomes turbid, showing the presence of carbon dioxide. The presence of two gases is thus indicated by the action of sulphuric acid on oxalic acid; the one an inflammable gas, the other a non-inflammable gas.

Fix up your apparatus in the same way as in the preparation of hydrogen (see fig. 22), only set your flask on a retort stand. Place about 10 grams of crystallised oxalic acid in the flask, add about 10 to 15 c.c. of strong sulphuric acid through the thistle funnel and heat the flask gently; allow time for the air to be displaced in the flask, then collect a jar of the mixed gases over the pneumatic trough. After you have collected a jar of the gases put the generating flask in a draught chamber, as the carbon monoxide is a very poisonous gas.

Experiment I.—Pour a little concentrated potassium or sodium hydrate solution quickly into the jar of the gas, cover its mouth, and shake briskly a few times. Invert the jar beneath the water in the trough and you will notice the water rise until it about half fills the jar.

$$CO_2 + CO + 2KOH = K_2CO_3 + H_2O + CO$$

Experiment II.—Decant the gas remaining from the last experiment into another smaller jar and apply a light to the mouth of the jar; the gas will burn with a pale lavender-blue flame. Allow the flame to go out, add a little clear limewater, and shake the jar; a turbidity will follow, indicating the presence of carbon dioxide.

$$CO + O = CO_2$$

Chlorine

Chlorine is a heavy gas, being about $2\frac{1}{2}$ times heavier than air, so that it can be collected by downward displacement.

Weigh out about 30 grams of manganese dioxide and about the same quantity of sodium chloride; mix them well together in a mortar, and transfer to a large flat-bottomed flask. Fix up your apparatus as for the preparation of carbon dioxide, but, if possible, use a caoutchouc cork; if not, give your cork a soaking in melted paraffin wax. Carefully pour down the thistle funnel dilute sulphuric acid (1 : 1); an action is at once set up, and the flask is filled by degrees with yellowish-green vapours, which pass over into the gas jar. Collect seven jars of the gas, and cover each jar with a well-greased cover-glass.

$$2NaCl + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$$

The preparation of chlorine should be conducted in a draught-chamber, as the inhaling of this gas causes irritation to the throat. If you do, by accident, happen to inhale any of it, pour a little alcohol on a piece of filter paper, place it over the nose and mouth, and breathe the vapour into the

lungs. If the gas should slacken off coming over into the jar, warm the flask a little.

Experiment I.—Invert a jar of the gas over the hole in the tray of a pneumatic trough filled with water, and remove the cover-glass; the water gradually rises in the jar, showing the solubility of chlorine in water.

Experiment II.—Moisten a piece of madder-dyed red cloth with water, put it in a jar of the gas, and place the cover-glass again over the mouth of the jar; the red cloth is gradually bleached.

Experiment III.—Pour a little concentrated sulphuric acid into another jar of the gas, and replace the cover-glass quickly, then shake the jar; after a short time put into the top of the jar a piece of dry madder cloth, similar to that used in the last experiment; it is not bleached. The gas in this experiment is dried by means of the sulphuric acid, and chlorine, when perfectly dry, does not bleach.

Experiment IV.—Take a small piece of filter paper, moisten it with turpentine, and plunge it into another jar of the gas; black smoke is at once seen in the jar, and a momentary flame; the filter paper is also charred.

$$C_{10}H_{16} + 16Cl = 16HCl + 10C$$

Experiment V.—Take a little finely powdered antimony, and shake it slowly into a jar of the gas; the antimony sparkles and burns as it passes through the gas.

$$Sb + 3Cl = SbCl_3$$

Experiment VI.—Place a piece of dry phosphorus in a deflagrating spoon, and pass it into a jar of the gas; the phosphorus takes fire, and burns with a brilliant flame.

$$P + Cl_3 = PCl_3$$

Experiment VII.—Into the remaining jar of the gas put two pieces of paper, one with letters printed on it with printers' ink, the other with letters written on it with ordinary ink; the printers' ink remains unchanged, while the ordinary ink is bleached. Printers' ink is essentially a mixture of carbon with some thickening material, while the ordinary ink partly consists of a vegetable substance containing a considerable amount of hydrogen in it.

Experiment VIII.—Put a little very finely powdered iron pyrites in a test-tube with some water, and pass a gentle stream of chlorine through the liquid. Keep the test-tube shaken all the time, to maintain the particles of iron pyrites in suspension. The pyrites after a time disappears, and only a few white particles are left floating about.

$$FeS_2 + 8H_2O + 14Cl = FeSO_4 + 14HCl + H_2SO_4$$
$$2FeSO_4 + H_2SO_4 + Cl_2 = Fe_2(SO_4)_3 + 2HCl$$

Filter the solution, and divide the filtrate into two portions. To the first portion add a little barium chloride; a dense white precipitate forms.

$$Fe_2(SO_4)_3 + 3BaCl_2 = Fe_2Cl_6 + 3BaSO_4$$

To the second portion add a slight excess of ammonium hydrate; a foxy-red precipitate forms.

$$Fe_2(SO_4)_3 + 6NH_4OH = Fe_2(OH)_6 + 3(NH_4)_2SO_4$$

Oxygen derivatives of Chlorine.

Use the apparatus employed in the preparation of chlorine, but with about half the quantity of manganese dioxide and sodium chloride in the flask. Make about 200 c.c. of a strong solution of potassium hydrate in a

beaker, surround the beaker with cold water, and pass a gentle stream of chlorine through the solution. After about five minutes remove the beaker, pour half its contents into another beaker, then set it on some wire gauze on a tripod over a bunsen flame, and continue to pass the chlorine through

$$2KOH + 2Cl = KClO + KCl + H_2O$$

the solution while it is boiling.

Take the cold portion of the potassium hydrate solution, notice its smell, it being different from that of chlorine, then perform the following experiments:—

Experiment I.—Take a piece of madder-dyed cloth, and dip it into the solution; the cloth is not bleached.

Experiment II.—Pour a small quantity of the solution into a test-tube, and add a few drops of hydrochloric acid; you notice an action going on, and chlorine is evolved.

$$KClO + 2HCl = KCl + H_2O + Cl_2$$

Experiment III.—Take the piece of madder-dyed cloth used in Experiment I. and dip it again into the solution, then pass it quickly through a dilute hydrochloric acid solution, and wash it in water; it is now bleached. By the action of the hydrochloric acid on the potassium hypochlorite (KClO) contained in the pores of the cloth, chlorine is liberated, and as the cloth is moist, it is bleached.

Place the remainder of the cold solution of potassium hypochlorite into a retort, add a little very dilute nitric acid, and attach to it a small receiver, then apply a gentle heat to the retort; a colourless peculiar-smelling liquid condenses in the receiver.

$$KClO + HNO_3 = KNO_3 + HClO$$

Take now the boiling solution of potassium hydrate through which chlorine has been passing for some time, transfer it to a porcelain evaporating dish, and evaporate it down to about half its original bulk; then allow it to cool. Crystals of potassium chlorate ($KClO_3$) separate out; drain off the liquid, and dry the crystals between pieces of filter paper.

$$6KOH + 6Cl = KClO_3 + 5KCl + 3H_2O$$

The potassium chloride (KCl) for the most part remains in solution, being more soluble than the chlorate.

Experiment IV.—Take one or two of the potassium chlorate crystals you have prepared, place them in a test-glass, cover them with water; put into the glass also a very small piece of phosphorus, and set a thistle funnel in the glass, so that its lower end just touches the crystals, as shown in fig. 32. Pour a few drops of strong sulphuric acid down the funnel; a greenish gas is evolved, which attacks the phosphorus so violently as to cause it to take fire under water. This gas is the peroxide of chlorine (Cl_2O_4).

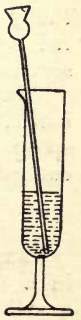

FIG. 32.

$$3KClO_3 + 2H_2SO_4 = KClO_4 + 2KHSO_4 + Cl_2O_4 + H_2O$$

Hydrochloric Acid.

Place a little sodium chloride in a test-tube and add a drop or two of strong sulphuric acid; an effervescence follows and a gas is given off with a strongly acid pungent odour.

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$

Set up your apparatus in the same way as for the preparation of carbon dioxide. Put about 20 grams of fused sodium chloride into the flask and pour through the thistle funnel sufficient strong sulphuric acid to cover the salt in the flask and collect the gas by downward displacement. To test when the jars are full, bring a lighted taper near the mouth; if it is extinguished remove the jar and cover it with a greased cover-glass. If the gas slackens in coming off, heat the flask gently. Collect two jars of the gas.

Experiment I.—Put a piece of blue litmus paper in a jar of the gas; it immediately turns red, showing the acid property of the gas.

Experiment II.—Invert the other jar of the gas and place it over the hole in the tray of a pneumatic trough filled with water, remove the cover-glass and you will see the water rise quickly in the jar, showing the solubility of hydrochloric acid gas.

Experiment III.—Take a few crystals of potassium bichromate, put them in a test-tube, and add a little strong hydrochloric acid, and heat; chlorine, which can be detected by its smell and colour, is evolved.

$$K_2Cr_2O_7 + 14HCl = Cr_2Cl_6 + 2KCl + 7H_2O + 6Cl$$

Bromine.

In the preparation of bromine, fix up your apparatus as for the preparation of nitric acid, surrounding the receiver with cold water. Mix about 4 grams of manganese dioxide with 2 grams of potassium bromide, transfer to the retort carefully, and add a little strong sulphuric acid; then replace the stopper in the retort and heat gently. Dark red fumes fill the retort, and a heavy dark red liquid condenses in the receiver. Collect a few c.c. of the liquid.

$$2KBr + 2H_2SO_4 + MnO_2 = K_2SO_4 + MnSO_4 + 2H_2O + Br_2.$$

Experiment I.—Take a few drops of bromine in a beaker and add about thirty times as much water; shake the mixture well, and a clear yellowish-red solution will be obtained. Dip a piece of madder-dyed cloth into this solution; it is bleached, but the action is slower than with chlorine.

Experiment II.—Pour a few drops of bromine into a wide-mouthed bottle, warm it gently, and plunge a piece of dry phosphorus on a deflagrating spoon into the bottle; light is evolved, the phosphorus combining so energetically with the bromine.

$$P + Br_3 = PBr_3$$

Experiment III.—Dissolve a few crystals of potassium bromide in water in a test-tube, add a little chlorine water, and shake; the water is turned a yellowish-red colour. Now add some carbon disulphide to the solution and shake well; the bromine is concentrated in the carbon disulphide.

$$KBr + Cl = KCl + Br$$

Iodine.

Mix about 1 or 2 grams of potassium iodide with about twice its weight of manganese dioxide, and transfer the mixture to a flask fixed on a retort stand, then add a few c.c. of strong sulphuric acid (do not fit a cork into

the flask); violet fumes soon appear, and condense in the neck of the flask, forming bright metallic-looking plates. Collect a few of these crystals.

$$2KI + MnO_2 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 2H_2O + I_2$$

Experiment I.—Take a crystal of iodine and shake it up with water in a test-tube; the water is slightly tinged yellow, but very little is apparently dissolved. To this solution add a little starch paste; a blue colour is at once produced. Heat this solution and the colour disappears, but reappears again on cooling. This test affords an easy means of detecting the presence of iodine.

Experiment II.—Dissolve a crystal of potassium iodide in water in a test-tube, add a few drops of starch paste; no blue coloration is produced. Add a drop or two of chlorine water; the blue colour instantly appears. Add more chlorine water, and the solution becomes colourless, owing to the formation of a chloride of iodine which has no action on starch.

$$KI + Cl = KCl + I$$
$$I + Cl = ICl$$

Experiment III.—Mix solutions of potassium iodide and bromide together in a test-tube, add carefully a little chlorine water; the liquid becomes a yellowish-red colour. Now add a little carbon disulphide and shake the tube; the iodine is dissolved in the carbon disulphide, giving it a violet colour. Draw off the solution from the carbon disulphide by means of a pipette, and to this solution add more chlorine water and carbon disulphide, and shake; the bromine is now dissolved, imparting to the carbon disulphide an orange colour. Iodine and bromine can thus be detected in the same solution.

Hydrofluoric Acid, Silicon Fluoride, and Hydrofluosilicic Acid.

Hydrofluoric acid can be prepared by the action of sulphuric acid on fluorspar (calcium fluoride), but glass apparatus cannot be used in the preparation on account of the action of this gas on the glass. Take a small round piece of sheet lead about 3 inches in diameter, and with the pestle press the centre of the lead in a mortar until you have made it cup-shaped. Into this leaden cup put about 5 or 6 grams of powdered fluorspar. Gently warm a glass plate large enough to cover the mouth of the leaden cup, and rub it over either with beeswax or paraffin, so that the plate is covered with a thin even coating of the wax; then trace some design on the glass plate with a sharp-pointed piece of wood or wire, making sure that the lines are drawn quite through the wax, and expose the glass. Now drench the fluorspar with strong sulphuric acid, and place the glass plate over the leaden cup, waxed side downwards, and warm the cup gently; white fumes come off and fill the cup. Allow these fumes to act upon the glass plate for a few minutes, then remove the plate and wash out the contents of the cup. Clean the wax off the glass plate with a cloth, and you will find the design etched into the glass.

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4$$
$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

The white fumes noticed in the cup are those of hydrofluoric acid, which attack the silica in the glass, forming Silicon tetrafluoride.

Silicon fluoride.—Fix up an apparatus similar to that used in the pre-

paration of carbon dioxide, allowing the flask to rest on a retort-stand. Into the flask put a mixture of about 10 grams of powdered fluorspar and 15 grams of fine sand; pour a little strong sulphuric acid down the thistle funnel, and shake the flask to mix the acid well with the mixture, then apply a gentle heat to the flask and collect the gas in a perfectly dry jar by downward displacement. To test when the jar is full bring a lighted taper into the mouth of the jar; if it is extinguished, cap the jar with a greased cover-glass.

$$2CaF_2 + SiO_2 + 2H_2SO_4 = 2CaSO_4 + 2H_2O + SiF_4$$

Experiment I.—Take a filter funnel large enough to rest in the mouth of the jar, and attach to it by means of a piece of caoutchouc tubing a small piece of glass tubing drawn out to a fairly fine point, as shown in fig. 33. Pour a little water into the funnel, remove the cover-glass from the jar and allow the funnel to rest in the mouth of the jar. As each drop of water falls from the opening of the narrow tube it seems to become solid, and a stalactite is formed on the end of the tube.

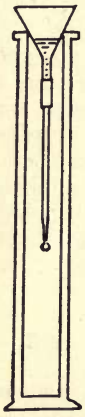

FIG. 33.

FIG. 34.

$$3SiF_4 + 4H_2O = H_4SiO_4 + 2H_2SiF_6$$

Experiment II.—Into a gas jar put a little mercury, and allow the delivery tube from the flask to dip just under the mercury (see fig. 34); then add a little water, heat the flask gently, and allow the gas to bubble through the mercury into the water; you will notice the silica separating out in the water. After the gas has been passed for a little time filter the water, and test it with a piece of blue litmus paper; it is turned red, showing the presence of an acid, which is hydrofluosilicic acid.

Sulphur Dioxide.

Fix up your apparatus as in the preparation of carbon dioxide, only set your flask on a retort-stand, so that it can be heated. Take about 20 grams of copper shavings or clippings and put them carefully into the flask, add through the thistle funnel about 60 c.c. of strong sulphuric acid, and heat up gradually until a brisk action goes on in the flask, then lower the flame. Collect three jars of the gas by downward displacement, and cover them with greased cover-glasses.

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$$

Experiment I.—Bring a lighted taper into a jar of the gas; the flame is extinguished, and the gas does not take fire.

Experiment II.—Put a few flowers (red, if possible) into another jar of the gas; the colour of the flowers after a little while is discharged, showing the gas possesses the property of bleaching.

Experiment III.—Invert the remaining jar of the gas beneath the water

in a trough, and remove the cover-glass; the water rises in the jar, showing the solubility of the gas. Place the hand beneath the mouth of the jar and remove it from the trough, then shake it briskly; again bring it under the water, and repeat this operation until the water has nearly filled the jar. Remove this jar with the water in it from the trough.

$$SO_2 + H_2O = H_2SO_3$$

Experiment IV.—Take a few c.c. of the solution prepared in the last experiment, add a little bromine water to it, and boil the mixture;

$$H_2SO_3 + 2BrH_2O = H_2SO_4 + 2HBr$$

add a few drops of barium chloride to a portion of the mixture; a white precipitate is thrown down, insoluble in hydrochloric acid, which indicates the presence of sulphuric acid.

$$H_2SO_4 + BaCl_2 = BaSO_4 + 2HCl$$

add to another portion of the mixture a little silver nitrate solution; a whitish precipitate is thrown down, indicating the presence of hydrobromic acid.

$$HBr + AgNO_3 = AgBr + HNO_3$$

Experiment V.—Take a few more c.c. of the solution from Experiment III. and add a drop or two of barium chloride; a white precipitate is thrown down; add a few drops of hydrochloric acid and the precipitate dissolves. Boil a few more c.c. of the sulphurous acid solution with a drop or two of nitric acid and then add barium chloride; a white precipitate is thrown down, insoluble in hydrochloric acid, showing a change in the original solution.

$$H_2SO_3 + O = H_2SO_4$$

Experiment VI.—Take a little potassium iodide solution in a beaker, add some water and a little starch paste, then one or two drops of chlorine water; an intense blue-coloured solution is produced. To this solution add, drop by drop, with constant stirring, sulphurous acid solution until the blue colour is entirely discharged. This bleaching is affected by the sulphurous acid taking up the oxygen from the water to form sulphuric acid, the hydrogen of the water combining with the iodine liberated from the potassium iodide, and forming hydriodic acid, which is colourless, soluble in water, and does not act on starch.

Sulphurous acid, you will observe, bleaches by *reduction*, while chlorine bleaches by *oxidation*.

Experiment VII.—Heat a few drops of sulphurous acid solution in a test-tube; a distinct smell of sulphur dioxide is given off.

Sulphur Trioxide.

Pour about 10 c.c. of strong Nordhausen sulphuric acid ($H_2S_2O_7$) into a small retort to which is attached a receiver; heat the retort carefully, and fumes of sulphur trioxide will pass over and condense to a white crystalline solid in the receiver.

$$H_2S_2O_7 = H_2SO_4 + SO_3$$

Allow a drop of water to fall on one of the crystals; the chemical combination is so intense that the water hisses as it does when falling on red-hot iron. If you test this solution you will find it is sulphuric acid.

$$SO_3 + H_2O = H_2SO_4$$

Heat a little strong sulphuric acid and pour it on to a small piece of sugar in a porcelain dish; the sugar is instantly charred; steam is given off, while a black mass of charcoal is left in the dish.

$$\underset{\text{(Sugar)}}{C_{12}H_{22}O} - 11H_2O = C_{12}$$

The sulphuric acid robs the sugar of its elements of water and leaves only carbon.

INSTRUCTIONS TO THE STUDENT.

The student has now obtained a fair knowledge of simple glass-working and of the preparation and properties of the more common gases. In the following sections he proceeds to examine solids and liquids (generally solids which are put into solution). First he examines an unknown substance by 'dry tests' for 'bases' and 'acids'; the results so obtained are then confirmed by systematic 'wet tests.'

The order of work laid down is to be followed with most careful and patient attention to all details; the student has then done his part, but unless this is supplemented by equal care on the part of the demonstrator, the best results cannot be expected. The demonstrator, besides supervising the actual testing, must prepare a carefully graded series of substances leading from simple salts containing one 'base' and one 'acid' to complex mixtures containing four or five 'bases' and several 'acids' (including insolubles). The substances must all be carefully selected with the definite object of teaching the student some important point in every mixture he analyses. Indiscriminate preparation of mixtures leads to waste of time and bad work.

In his first tests the student may be given salts of known composition, and his work is then checked by unknown salts from the demonstrator's set. For instance, on the next page he may take $ZnCl_2$, $SnCl_2$, Pb, Bi_2S_3, and so on for practice, and when fairly confident, his proficiency or otherwise is checked on 'unknown' salts given by the demonstrator.

The demonstrator's 'Record Book' should show full details of the substances given to each student, the results obtained, the time taken with the analysis, and general remarks where necessary. A somewhat similar record must be kept of the work done in Quantitative Analysis and Assaying.

CHAPTER III

PRELIMINARY EXAMINATION FOR BASES

Experiment.	Observation.	Inference.
1. Heat the substance in a tube closed at one end.	1. Substance decrepitates.	Chlorides, nitrates, etc.
	2. Changes colour—	
	Yellow while hot to white on cooling.	**ZnO.**
	Yellowish brown while hot to dirty yellow on cooling.	**SnO.**
	Reddish brown while hot to yellow on cooling.	**PbO.**
	Orange brown while hot to dull yellow on cooling.	**Bi_2O_3.**
	Dark red while hot to reddish brown on cooling.	**Fe_2O_3.**
	Dark red while hot to yellow on cooling.	**K_2CrO_4.**
	3. Substance does not change colour, but fuses and solidifies on removal from the flame.	Salts of the alkalies and alk. earths.
	4. Fumes are evolved and a sublimate is formed.	**NH_4, Hg, As, Sb_2O_3, S, I.**
	(*a*) With odour of frankincense.	Benzoic acid.
	(*b*) Irritating fumes, causing coughing.	Succinic acid.
	Note.—If a sublimate be obtained, mix the substance with twice its bulk of a mixture of **Na_2CO_3 + KCN**, and heat in a fresh closed tube.	
	(*a*) Metallic mirror and globules of metallic mercury.	**Hg.**
	(*b*) A black shining mirror and no globules.	**As.**
	5. Brown fumes of **N_2O_4** and **O_2** are evolved.	Nitrates of **Pb, Bi**, etc.
	6. Substance chars and evolves odours of burning organic matter.	Organic acids.
	7. If no change takes place, the absence of all the above is indicated.	
2. Heat the substance on charcoal before the blowpipe.	1. Substance decrepitates.	Chlorides, etc.
	2. Substance deflagrates.	Nitrates, chlorates.
	3. Substance fuses and is absorbed by the charcoal or forms a fluid bead.	Salts of the alkalies, etc.
	4. An infusible white residue is left, highly luminous when heated. When residue is cold, moisten with **$Co(NO_3)_2$** and reheat strongly.	**BaO, SrO, CaO, MgO, ZnO, Al_2O_3, SiO_2.**
	(*a*) A pale pink coloured mass is left.	**MgO.**
	(*b*) A green coloured mass is left.	**ZnO.**
	(*c*) A blue coloured mass is left.	**Al_2O_3,** Phosphates, arsenates, **SiO_2.**
	(*d*) A bluish green coloured mass is left.	**SnO_2.**

Experiment.	Observation.	Inference.
	5. A coloured residue is left. Heat a little of the substance in a borax bead first in the *oxidising flame* then in the *reducing flame*.	
	O.F.— R.F.—	
	Green when hot, blue when cold, Red.	**Cu.**
	Blue, ... Blue.	**Co.**
	Yellow to brown, . . . Turbid grey.	**Ni.**
	Yellow to brownish red, . . Bottle-green.	**Fe.**
	Amethyst, ... Colourless.	**Mn.**
	Green, ... Green.	**Cr.**
	Note.—If **Mn** or **Cr** be indicated, heat the substance on **Pt** foil with 4(Na_2CO_3 + KNO_3).	
	(*a*) Yellow mass.	**Cr.**
	(*b*) Bluish green mass.	**Mn.**
3. Heat the substance with four times its bulk of Na_2CO_3 + **KCN** on charcoal in the reducing flame.	1. A white incrustation is formed on the charcoal.	$HgCl_2$ and Sb_2O_3.
	A white incrustation is formed on the charcoal with garlic odour.	**As.**
	An incrustation—	
	Yellow while hot, white when cold.	**Zn.**
	Reddish brown, readily volatilised.	**Cd.**
	2. Metallic beads are formed—	
	(*a*) With incrustation.	
	White malleable beads, incrustation.	
	Hot. *Cold.*	
	Yellow to white.	**Sn.**
	Bluish white beads which mark paper.	
	Incrustation—	
	Hot. *Cold.*	
	Orange to yellow.	**Pb.**
	White brittle beads, copious white fumes, and incrustation.	**Sb.**
	White brittle beads. Incrustation—	
	Hot. *Cold.*	
	Dark orange to yellow.	**Bi.**
	(*b*) Without incrustation.	
	White malleable metallic beads.	**Ag.**
	Yellow ,, ,, ,,	**Au.**
	Red ,, ,, ,,	**Cu.**
	Black magnetic infusible powder.	**Fe, Ni, Co.**
	3. Place part of fused mass on a silver coin and moisten with water.—Black stain.	**S** in form of sulphide or sulphate.
4. Heat the substance on **Pt** wire with **HCl** in a Bunsen flame.	The flame is coloured—	
	Bright yellow.	**Na.**
	Lavender.	**K.**
	Apple green.	**Ba.**
	Crimson.	**Sr.**
	Brick red.	**Ca.**
	Green.	**Cu.**
	Livid blue.	$CuCl_2$, **As, Sb, Bi, Pb, Sn, Hg.**
5. Heat the substance in a test-tube with **NaOH** solution.	Smell of ammonia.	NH_4 compounds.
6. Heat substance in a bead of microcosmic salt.	An undissolved residue.	SiO_2.

PREPARATION OF SOLUTION FOR BASES.

1. Boil the finely-divided substance in distilled water.

2. If insoluble, add $\frac{1}{4}$ its bulk of strong **HCl** and boil for two or three minutes.

3. If still insoluble, treat a fresh portion with strong **HCl** and boil for five minutes; then add an equal volume of water and warm.
The majority of substances will dissolve with the above treatment.

4. If there is still an insoluble residue, decant off the solution from (3), add a little fresh **HCl**, boil, then add strong HNO_3, drop by drop, as long as the substance appears to dissolve (about 6 drops should suffice).
Certain sulphides and a few other compounds are dissolved by this treatment.
If no action occurs on treating thus, decant off the acid and neglect it. Wash the insoluble residue and treat by table for insolubles.

5. Insoluble double cyanides (indicated by a strongly-coloured insoluble) require special treatment by fusing in a porcelain crucible with three times their bulk of NH_4NO_3 and $(NH_4)_2S_{11}O_4$ (1 : 3) in a fume chamber, dissolving in **HCl** and treating as usual. (**Ba, Sr, Pb** will remain insoluble; **As** and **Hg** may be volatilized.)

6. Metals or alloys should be in a fine powder or in thin sheets.
(*a*) Obtain solution as usual.
(*b*) If solution is slow, treat with dilute HNO_3 and, if still slow, with strong HNO_3; dilute and filter.

Residue.—Au, Pt, SnO_2, Sb_2O_4, **Sn** (as arsenates), **Bi** (as arsenate or phosphate). Test for **Au** and **Pt** separately in Aqua Regia solution.

Warm with $(NH_4)_2S$ and filter.

Residue.—Bi_2S_3.	**Solution.—As, Sb, Sn** as thio salts. Examine by Table II. (2nd part). Test for H_3PO_4 after the removal of the **As, Sb,** and **Sn.**

If the original residue is white, probably only Sb_2O_4 and SnO_2 are present. Boil with strong tartaric acid and filter.

Residue.—SnO_2. Reduce on charcoal with **KCN** and Na_2CO_3.	**Solution.—**Contains the **Sb.** Pass H_2S = Orange **p'p't.**

Note 1. If much **HCl** has been used to obtain a solution, evaporate nearly to dryness and add H_2O.

Note 2. If HNO_3 has been used to obtain a solution, add strong **HCl** and evaporate nearly to dryness to drive off HNO_3 and then dilute with H_2O.

Note 3. The solution should be free from HNO_3 and not contain much **HCl.**

NOTES ON THE PREPARATION OF SOLUTION FOR BASES.

The substance is first treated with distilled water, boiled, and then allowed to cool; if it is not all soluble, some of the clear solution is decanted off and tested with **HCl** (bench reagent) for presence of Group I.

If Group I. is present, the whole of the water solution must be filtered off and **HCl** added to it; the solution is then added to the insoluble residue, together with a few drops of strong **HCl** and boiled for three minutes; if a residue still remains, the dilute **HCl** solution is filtered off and the residue treated with a little strong **HCl**. If soluble, the strong **HCl** solution is added to the dilute **HCl** solution; but if there is still a residue it is treated with fresh **HCl**, boiled, and HNO_3 added, drop by drop, as long as the substance appears to dissolve.

If HNO_3 has been used to get the substance into solution, it has to be expelled before proceeding by the group tests; therefore it is advisable to keep this solution as small as possible.

If insoluble double cyanides are present in the substance to be treated, a solution in the ordinary way should be obtained and treated as far as possible, besides the solution obtained after decomposing the double cyanides.

NOTES TO THE GENERAL TABLE.

1. If **Cr** has been indicated in the preliminary, and the solution has a yellow or orange colour, chromates or bichromates may be present and must be reduced to chromic salts; therefore, after adding **HCl**, add alcohol and boil till the odour of aldehyde or alcohol is dispelled before passing H_2S.

2. If cyanogen was detected in the preliminary, test original for double cyanides before proceeding in the usual way.

3. If **I** or **Br** is present the solution should be boiled with Aqua Regia before passing on to Group II.

4. If the original substance had to be dissolved in **HCl** and did not require the application of Notes 1, 2, or 3, H_2S may be passed at once.

5. **HCl** will produce a p'p't in a saturated solution of a **Ba** salt, soluble in hot water. From alkaline solutions **HCl** precipitates gelatinous H_4SiO_4, crystalline p'p'ts of boric, benzoic, and uric acids, also amorphous Sb_2O_5, metallic oxides as Al_2O_3, and sulphides, As_2S_3, Sb_2S_3, Sb_2S_5, SnS, SnS_2 (soluble in **NaOH** and $(NH_4)_2S_2$ and precipitated by dilute **HCl**).

These oxides and sulphides are best examined separately.

6. If **As** has been detected in the preliminary, this filtrate, which may contain pentad **As**, should be boiled with H_2SO_3 and the acid solution evaporated considerably to expel SO_2. **Ba**, **Sr**, or **Pb**, if present, may be precipitated, partially or wholly, as sulphates, and the p'p't should be examined separately.

7. Oxychlorides of **Bi**, **Sb**, and **Sn** may be precipitated on the first

[*Continued on p.* 30.

Notes (1), (2), (3).—To greater part of the solution add **HCl** while p'p't forms, warm, filter, and wash (4).

<table>
<tr><td>P'p't: (5) Group I.</td><td colspan="4">Filtrate.—(6) dilute largely, (7) saturate with H_2S, warm, filter (8) and (9).</td></tr>
<tr><td>$PbCl_2$ White
AgCl ,,
Hg_2Cl_2 ,,

Exam. by Table I.</td><td>P'p't: Group II.

HgS Black
PbS ,,
Bi_2S_3 ,,
CuS ,,
CdS Yellow
SnS Brown
SnS_2 Yellow
Sb_2S_3 Orange
Sb_2S_5 ,,
As_2S_3 Yellow
Au_2S_3 Black
PtS_2 ,,

Exam. by Table II</td><td colspan="3">Filtrate.—Boil off H_2S, add 3 drops of strong HNO_3 and boil; if SiO_2 be suspected, evaporate to dryness. If organic matter (10) or oxalate be suspected (indicated by blackening of residue (11)), heat to redness in a porcelain dish. Add to residue a little strong HCl, then H_2O, warm (a white residue of SiO_2, see (12)). Test 5 drops of this solution for H_3PO_4 with strong HNO_3 and $(NH_4)_2MoO_4$, warm.

(1) No p'p't=H_3PO_4 absent. Exam. by A.
(2) Yellow p'p't=H_3PO_4 present. Exam. by B.

A

Add NH_4Cl in excess, warm, add excess of NH_4HO, filter quickly and wash with hot H_2O.

<table><tr><td>P'p't: (13) Group IIIa.

$Fe_2(HO)_6$ red.
$Cr_2(HO)_6$ dirty green.
$Al_2(HO)_6$ white gelatinous.

Exam. by Table IIIa.</td><td colspan="2">Filtrate.—Pass H_2S.

<table><tr><td>P'p't: Group IIIb.

ZnS white
MnS flesh colour
NiS black
CoS ,,

Exam. by Table IIIb.</td><td>Filtrate. — Add $(NH_4)_2CO_3$ and warm (14).

<table><tr><td>P'p't: Group IV.

$BaCO_3$ white
$SrCO_3$,,
$CaCO_3$,,

Exam. by Table IV.</td><td>Filtrate. Group V.

Mg
K
Na

Exam. by Table V.</td></tr></table></td></tr></table></td></tr></table>
B

Add NH_4Cl in excess, warm, and add excess of NH_4HO, filter quickly, wash with hot H_2O.

<table><tr><td>P'p't: (13).

Fe, Cr, Al Hydrates.
Fe, Cr, Al, Zn, Mn, Ni, Co, Ba, Sr, Ca, Mg Phosphates.

Exam. by Table IIIc.</td><td>Filtrate.

Proceed exactly as in A.</td></tr></table></td></tr>
</table>

addition of HCl (dilute) or water, but are readily dissolved in more acid on gently heating.

8. H_2S often produces merely a precipitation of S, owing to presence of oxidising agents, as Cl, Br, I, HNO_3, HClO, $HBrO_3$, and H_2CrO_4 or ferric salts, also H_2SO_3, etc. This p'p't is white and remains suspended in the solution; it should be filtered off and neglected. In strongly acid solutions a brick-red p'p't of $PbSCl_2$ often comes down; if so, dilute largely. Cd is often left in solution if too much acid is present.

9. Pass H_2S again through filtrate (diluted further) to insure complete precipitation.

10. Organic acids, *e.g.* citric and tartaric, also sugar, prevent the precipitation of $Al_2(OH)_6$.

11. Organic acids should be detected in the preliminary. If they are absent it is not necessary to heat to redness.

12. This SiO_2 may be mixed with other substances, Al_2O_3, Cr_2O_3, Fe_2O_3, rendered insoluble by strong ignition; $BaSO_4$ and $SrSO_4$; examine separately.

13. Small quantities of the borates and fluorides of the alkaline earthy metals may be precipitated here, but need not be examined further, since their bases will be detected in Group IV., and their acids on examination in the usual way.

14. The solution must not be boiled, because the NH_4Cl present would convert the carbonates into soluble chlorides, the CO_2 volatilizing as ammonium carbonate.

TABLE I.

Separation of Group I.

<table>
<tr><td colspan="3">P'p't: $PbCl_2$, AgCl, Hg_2Cl_2 (also H_3BO_3, H_4SiO_4, $H\overline{U}$, $H\overline{Bz}$). Wash, precipitate on filter with hot H_2O till all $PbCl_2$ is dissolved out.</td></tr>
<tr><td colspan="2">Residue.—AgCl, Hg_2Cl_2.—Wash with warm dil. NH_4HO.</td><td>Filtrate.—Cool. Acicular crystals of $PbCl_2$ fall out.
Add $K_2Cr_2O_7$.
Yellow p'p't.
Pb.</td></tr>
<tr><td>Residue.—Black NH_2Hg_2Cl. Dry and heat with Na_2CO_3 in closed tube.
Metallic Mirror.
Hg.</td><td>Filtrate.
Acidify with HNO_3.
White curdy p'p't.
Ag.</td><td></td></tr>
</table>

Separation of Group II.

P'p't: HgS, PbS, Bi_2S_3, CuS, CdS, SnS, SnS_2, Sb_2S_3, Sb_2S_5, As_2S_3 (Au and Pt must be tested for separately in filtrate from Group I.).
Wash p'p't., boil with **NaOH**, filter.

Residue.—Wash, boil with dilute HNO_3, dilute, and if **Pb** is present add dilute H_2SO_4 and an equal bulk of C_2H_5OH.

Residue.—**HgS, S, PbS, $PbSO_4$.** Boil with $NH_4\overline{A}$, cool and filter.

Residue.—**HgS** and **S** or **S** alone. Dissolve in Aqua Regia, dilute largely add a bright strip of copper. A silvery deposit on Copper.

Hg.

Solution.—Add $K_2Cr_2O_7$. Yellow p'p't.

Pb.

Solution.—Boil off C_2H_5OH till pasty dilute, add excess of NH_4OH, boil and filter.

Residue. — Bi_2O_3, $3H_2O$ dissolve in little **HCl**, and pour solution into a beaker of water. White p'p't.

Bi.

Solution.—Blue if **Cu** is present. Add solution of **KCN** till colourless. Pass H_2S and filter.

Residue. Yellow.

Cd.

Solution. Boil with dilute HNO_3 till H_2S is expelled. Add excess NH_4HO then $H\overline{A}$ till acid and $K_4Fe(CN)_6$ Brown p'p't.

Cu.

Filtrate.—**As, Sb, Sn (Au, Pt.)** as sulpho-salts. Acidulate with **HCl** (dil.) sulphides are reprecipitated. Filter and wash. Digest p'p't: with conc. **HCl**.

Residue. — As_2S_3. Reduce in bulb tube with Na_2CO_3 + **KCN**. Metallic mirror and garlic odour.

As.

Solution.—Cool, dilute, place in a dish with **Pt** and **Zn** in contact and let reaction go on.

Pt.—Black Stain. Dissolve in HNO_3, add **HCl**, dilute, pass H_2S. Orange p'p't.

Sb.

Zn.—Scrape off black surface and dissolve scrapings in **HCl** (as little as possible). Filter, add $HgCl_2$ to clear solution. White or grey p'p't.

Sn.

Note.—If **HgS** be present, dissolve in $(NH_4)_2S$ instead of **NaOH**. **HgS** is partly soluble in **NaOH**. A little **CuS**, if present, will be dissolved by the $(NH_4)_2S$.

TABLE IIIa.

Separation of Group IIIa.

P'p't: $Al_2(HO)_6$, $Cr_2(HO)_6$, $Fe_2(HO)_6$.
Wash with hot water, dissolve in dil. **HCl**, add **NaOH** till strongly alkaline.
(1) Boil for some minutes, filter off (moisten filter paper first).

Residue.—Dry and fuse with $Na_2CO_3 + KNO_3$ on Pt foil; transfer to test-tube, and boil with H_2O. Filter.

Residue.—Dissolve in dilute **HCl** and add $K_4Fe(CN)_6$.
Blue p'p't:
Fe.
Test original **HCl** solution for **Fe″** or **Fe‴** by $K_6Fe_2(CN)_{12}$ and $K_4Fe(CN)_6$ or **KCNS.**

Solution.—Yellow. Acidify with **HA**, add $Pb\bar{A}_2$.
Yellow p'p't:
Cr.
(2) Chromate, if present, will be found in testing for acid in Na_2CO_3 solution.

Solution.—Acidify with **HCl**, add NH_4HO in slight excess.
White gelatinous p'p't:
Al.

Note 1. The **NaOH** should contain no Al_2O_3; if it does, test a similar amount by acidifying with **HCl** and adding NH_4HO. Compare this p'p't with one obtained.
Note 2. Traces of **Mn** may appear here, indicated by bluish green mass changing to purple in solution.

TABLE IIIb.

Separation of Group IIIb.

P'p't: (1) **ZnS, MnS, NiS, CoS.**
Wash, dissolve in **HCl**, using a crystal or two of $KClO_3$ if necessary. Evaporate off **Cl**, filter off any **S**, warm for about five minutes with **NaOH**, filter.

Residue.—$Mn(OH)_2$, $Ni(OH)_2$, $Co(OH)_2$. Wash, dissolve in **HCl**, nearly neutralise with NH_4OH, add $NH_4\bar{A}$ in excess. Pass H_2S for several minutes.

Residue.—**NiS, CoS.** — Test in borax bead. Yellow to sherry-red bead = **Ni** with no **Co**. If blue bead, **Co.** alone or with **Ni.**— Then dissolve in hot **HCl** + $KClO_3$, boil off **Cl**, neutralise with Na_2CO_3, add excess of solution of **KCN** in cold H_2O, till p'p't is all dissolved. Add **NaOH** till strongly alkaline and 2 vols. of **Br** water; warm, allow to stand, filter.

P'p't: Black. Ni_2O_3. Test in borax bead.

Solution.— Evaporate to dryness, and test in borax bead.
Blue.
Co.

Solution.—$Mn\bar{A}_2$. Add Na_2CO_3. Dissolve p'p't in **HCl**, add NH_4Cl, NH_4HO and pass H_2S.
Pink p'p't:
Mn.

Solution. — **Zn** as Na_2ZnO_2. Pass H_2S.
White p'p't:
Zn.

Note 1. If p'p't is not black, no **Ni** or **Co** need be looked for. If black p'p't passes through filter, **Ni** is nearly certain to be present.

TABLE IIIc.

Separation of Phosphates.

P'p't: $Al_2(HO)_6$, $Fe_2(HO)_6$ and **Al, Cr, Fe, Zn, Mn, Ni, Co, Ba, Sr, Ca** and **Mg** as phosphates.
Dissolve in **HCl**, neutralise with solid Na_2CO_3 till p'p't just formed, dissolve in one or two drops of **HCl**. Add solution of $Na_2\bar{A}$ and $H\bar{A}$. Filter.

Residue. — Al, Cr, Fe as phosphates. Exam. by Table IIIa.

Solution. — Al and **Cr** chlorides, **Zn, Mn, Ni, Co, Ba, Sr, Ca, Mg** phosphates. Remove the H_3PO_4, by adding Fe_2Cl_6 drop by drop as long as a p'p't falls (as soon as a yellow colour appears **Fe** acetate is being formed, in which **Fe** phosphate is soluble); boil and filter.

Residue. — Fe phosphate and basic acetate.

Neglect.

Solution.—Chlorides only (test if any H_3PO_4 is present with a drop of Fe_2Cl_6 in a small portion). Add NH_4Cl and NH_4HO as in General Table; filter.

Residue.— Group IIIa.

Solution.—Pass H_2S and filter.

Residue.— Group IIIb.

Solution. — Add $(NH_4)_2CO_3$ and warm; filter.

Residue.— Group IV.

Solution.—Add Na_2HPO_4 and allow to stand five minutes. White p'p't: **Mg.**

TABLE IV.

Separation of Group IV.

P'p't: $BaCO_3$, $SrCO_3$, $CaCO_3$.
Dissolve in **HCl** and divide into two portions.

1st Portion.

Add $CaSO_4$.
Immediate p'p't: **Ba.**

2nd Portion.

Add NH_4OH and $H\bar{A}$ till acid, then $K_2Cr_2O_7$.

Yellow p'p't: **Ba.** Confirm.

Solution.—Add K_2SO_4.

P'p't: $SrSO_4$. Confirm.

Solution.—Add NH_4OH excess and $(NH_4)_2\bar{O}x$.
White p'p't: CaC_2O_4. Confirm.

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TABLE V.

Separation of Group V.

If **Ba**, **Sr** or **Ca** are present, add 2 drops of $(NH_4)_2\overline{Ox}$ and 2 drops of $(NH_4)_2SO_4$.

Solution.—$MgCl_2$, **KCl**, **NaCl** (1).

Take about ¼ of the solution and add Na_2HPO_4. Warm gently and allow to stand. White p'p't: **Mg**.	Evaporate remainder to dryness in a porcelain dish, and ignite till all fumes disappear and all amm. salts are driven off.	
	Dissolve part in water, add $PtCl_4$ and evaporate till pasty, add a drop of **HCl** and a little C_2H_5OH. Yellow crystalline p'p't: **K**.	To rest add a drop of conc. HNO_3, and test in bunsen flame on Pt wire. Yellow flame. **Na**.

Note.—Always test for NH_4 in the original substance by boiling with **NaOH**; NH_3 evolved indicates NH_4 present.

PRELIMINARY EXAMINATION FOR ACIDS.

Experiment.	Observation.	Inference.
1. Warm the substance in a test-tube with dilute **HCl**.	* Gases are given off. A colourless gas with faint smell is given off, which precipitates lime or baryta water.	CO_2 from carbonates.
Confirm for SO_2 by passing gas through acidulated K_2CrO_4 solution.	* Ditto, having suffocating odour of burning sulphur.	SO_2 from sulphites.
	* Ditto, with precipitation of sulphur.	SO_2 from hyposulphites.
Confirm for H_2S with lead acetate paper.	* Ditto, with odour of rotten eggs.	H_2S from sulphides except Au_2S_3, PtS_2, Ag_2S, HgS, CuS, Bi_2S_3, As_2S_3. These, however, give off H_2S in presence of **Zn** and **HCl**.
	* Ditto, with odour of bitter almonds.	**HCN** from cyanides.
	Reddish brown fumes.	N_2O_3 from nitrites.
	A yellow green gas of suffocating odour, which bleaches indigo and other vegetable colours.	**Cl** from hypochlorites, also from reaction of H_2CrO_4 upon **HCl**.
2. Heat a portion of the substance with dilute H_2SO_4 (1 : 1).	Gases are given off.	CO_2, H_2S, SO_2, N_2O_3, and **HCN** have already been detected by means of dilute **HCl**.
	Smell of vinegar.	Acetate.
	Strong acid fumes.	**HCl**, **HF** (**HCN** from ferro- and ferricyanides), $H_2S_2O_3$, **HClO**, **HCNO**.
Confirm for **HCN** by allowing the gas to act upon $(NH_4)_2S$ on a watch-glass, and adding Fe_2Cl_6.	Blood-red coloration.	**CN**: compounds.
	No gases or vapours are evolved.	SiO_2, B_2O_3, P_2O_5, SO_3, I_2O_5, As_2O_5, TiO_2, may be present.

PRELIMINARY EXAMINATION FOR ACIDS—*continued.*

Experiment.	Observation.	Inference.
3. Warm with a few drops of H_2SO_4 (the heat must not be sufficient to drive off the H_2SO_4).	Colourless gases or fumes evolved.	
Confirm for **HCl** by heating with MnO_2; **Cl** evolved.	With irritating odour, gives white fumes with NH_3.	**HCl.**
Confirm for **HF** by etching glass after waxing part of the surface.	Corrode glass.	**HF.**
	CO evolved with blackening.	Formic acid.
Remove CO_2 by passing through **KOH** solution and burn the **CO.**	**CO** and CO_2 evolved.	Oxalic acid.
	Peculiar odour, mixture of H_2S, SO_2 and **HCN** with precipitation of **S**; fumes redden, paper moistened with Fe_2Cl_6.	Sulphocyanides.
	CO, CO_2 and SO_2 and odour of burnt sugar; substance also blackens (tartaric acid chars rapidly, citric acid but slowly).	Tartaric and citric acids.
	Oxygen evolved.	Chromates, permanganic acid, peroxides and other easily decomposed compounds rich in **O.**
	Coloured gases are evolved — violet vapours, turn starch paper blue.	Iodides (and iodates in presence of reducing agents).
	Reddish-brown vapours which turn starch paper yellow.	**Br.**
	Greenish-yellow gas with small explosions.	Chlorates.
Confirm for HNO_3 by adding a fragment of **Cu**;—fumes become red.	Brownish-yellow irritating vapours.	Nitrates.
	On treating with acids, amongst substances which may separate out are—	
	White sulphur (with H_2S).	From polysulphides.
	Yellow ,, (,, SO_2).	From thiosulphates and polythionates.
	Iodine.	From iodides in presence of oxidising bodies, and from iodates in presence of reducing bodies.
Confirm for Silica by fusing in $NaNH_4HPO_4$ bead—Silica skeleton.	Colourless gelatinous silica.	From silicates.
	Yellow (when hot).	Tungstic acid, from tungstates.
	White molybdic acid, soluble in an excess of acid.	
	Boracic, benzoic, succinic, uric and other acids separate out from concentrated solutions.	
4. Heat in porcelain crucible lid.	Chars much, and gives off odour of burnt sugar.	Tartrate or citrate.
	Chars slightly.	Oxalate, acetate, or other organic acid.

EXAMINATION OF SOLUTION FOR ACIDS.

If any metals are present, which give reactions with reagents which are to be added, boil with Na_2CO_3 (if insoluble salts are present use **NaOH** also). Filter off precipitated metals, divide into four portions.

1. Acidify with HCl and heat. Divide into 2.

1. Add $BaCl_2$—**White p'p't.** H_2SO_4 insol. in acids.

   H_2SiF_6 give gelatinous p'p't. On boiling this p'p't SiF_4 is evolved.

2. Add Fe_2Cl_6—**Blue p'p't.** $H_4Fe(CN)_6$.

   Red Colour. HCNS.

   Filter off any p'p't and add $SnCl_2$.

   Blue p'p't. $H_6Fe_2(CN)_{12}$.

2. Acidify with HNO_3.

Add $AgNO_3$—

White p'p't (sol. in NH_4OH) } HCl, HCN, $H_6Fe_2(CN)_{12}$

Yellow - white p'p't sol. with difficulty in NH_4OH.

HBr.

Insol. in NH_4OH } HI. yellow. HCNS, white. $H_4Fe(CN)_6$,,

HCN, $H_4Fe(CN)_6$, $H_6Fe_2(CN)_{12}$, and HCNS should have been detected.

HBr and HI may be confirmed in original by Cl water and CS_2.

HBr, orange colour.

HI, violet ,,

HCl in the presence of HBr and HI may be detected by mixing the powdered substance with $K_2Cr_2O_7$ (powdered) and warming gently with strong H_2SO_4—a red-brown vapour is given off, CrO_2Cl_2, which can be absorbed by NH_4OH or alkaline hydroxides. The yellow colour with NH_4OH indicates the presence of a chloride.

3. Acidify with $H\overline{A}$. Divide into 3.

1. Add $CaCl_2$—**White p'p't.** $H_2\overline{Ox}$, HF or H_2SO_4. Ignite p'p't. $H_2\overline{Ox}$ leaves a carbonate which effervesces with acids. HF and H_2SO_4 are unchanged.

2. Add $Pb\overline{A}_2$—**Yellow p'p't** = $H_2\overline{CrO}_4$.
   White p'p't = H_2SO_4.

3. Add Fe_2Cl_6—**Yellow-white p'p't.** H_3PO_4 or H_3AsO_4.
   Remove As by H_2SO_3 and H_2S before boiling with Na_2CO_3, and then test for H_3PO_4.

4. Expel CO_2 by HNO_3, neutralise with NH_4HO, boil off NH_3 and divide into 2.

1. Add excess of $CaCl_2$—**White p'p't,** at once insol. in $H\overline{A} = H_2\overline{Ox}$.
   White p'p't: after 5 mins' shaking = $H_2\overline{T}$.
   White p'p't: only after boiling some time = $H_3\overline{Ci}$.
   White p'p't: only after adding 3 vols. of $C_2H_5OH = H_2\overline{Su}$.

2. To quite neutral solution add Fe_2Cl_6.
   Pale yellow p'p't = $H\overline{Bz}$.
   Red brown p'p't = $H_2\overline{Su}$.
   Red brown p'p't or red colour, = $H\overline{Fo}$.
   Confirm by warming H_2O solution of original with $HgCl_2$.
   White p'p't = $H\overline{Fo}$.
   Red colour destroyed by $HCl = H\overline{A}$.

Note 2.

Note 1. Do not boil with Na_2CO_3 unless necessary. If only alkalies are present it is unnecessary.

Note 2. If organic acids and Groups I. and II. or H_2CrO_4 are present add **HCl**, and pass H_2S before boiling with Na_2CO_3 to make solution (4).

The following should be tested for separately :—

HNO_3.—Black ring test, with solution of $FeSO_4$ and H_2SO_4. H_3BO_3.—To a little of the substance in a watch-glass add strong H_2SO_4, then C_2H_5OH; apply a light. If alcohol burns with a green-edged flame = H_3BO_3. HF.—Sand and H_2SO_4 test.

TABLE FOR ANALYSIS OF INSOLUBLE SUBSTANCES.

The insoluble residue remaining after treating with acids should be thoroughly washed and then dried. It may contain the following substances—C, S, AgCl, SiO_2 and Silicates, $BaSO_4$, $SrSO_4$, Al_2O_3, Cr_2O_3, Chrome Iron ($FeO.Cr_2O_3$), CaF_2, SnO_2, Sb_2O_4. The following also may be present, but should be found in solution as well—$PbCl_2$, $PbSO_4$, $CaSO_4$, Fe_2O_3.

A careful preliminary examination should be made first. Some of the above may be dissolved out by special solvents, and tested for in the filtrate, thus :—

$PbCl_2$ is soluble in hot water.
$PbSO_4$ is soluble in ammonium acetate.
AgCl is soluble in NH_4OH or KCN.

After these preliminary tests, mix the dry substance with from three to four times its bulk of fusion mixture ($Na_2CO_3 + K_2CO_3$) and fuse on Pt foil (Ag and Pb must first be removed) until the mass is in tranquil fusion. Boil up with hot-water, filter.

<table>
<tr><td colspan="2">Residue.—Contains the bases; dissolve in HCl, filter and wash.</td><td colspan="2">Filtrate.—Contains the acids (sometimes a little Al and Sn compounds). Acidify with HCl, evaporate to dryness, take up with HCl and filter.</td></tr>
<tr><td>Residue. — SnO_2, Sb_2O_4, CaF_2 (white) and Chrome Iron (black).
Sb_2O_4 may be dissolved out by H_2T, and tested for by H_2S.
SnO_2 must be detected in the dry way.
CaF_2 gives Ca flame and F reaction.
Chrome Iron gives green Borax bead of Cr.</td><td>Filtrate. Examine for Bases mentioned above in the usual way.</td><td>Residue. SiO_2</td><td>Filtrate. — Examine for the following acids as usual. H_2SO_4, H_2CrO_4, HF (these are best identified by special test).
H_3PO_4 and H_3AsO_4 are sometimes left in an insoluble, and will be found here.</td></tr>
</table>

Name of Reagent.	Symbol.	Molec. Weight.	Equivalent Weight.	Grams per litre.	Strength.	Method of preparing Reagent.
Sulphuric acid.	H_2SO_4	98	49	...	36 E	Sulphuric acid, sp. gr. 1·8427, at 15·5° C.
,, ,,	,,	,,	,,	...	5 E	,, ,, diluted to sp. gr. 1·1527, at 15·5° C.
,, ,,	,,	,,	,,	49	E	200 c.c. of 5 E sulphuric acid diluted to 1 litre.
Nitric acid.	HNO_3	63	63	...	24 E –	Nitric acid, sp. gr. 1·50.
,, ,,	,,	,,	,,	...	16 E	,, ,, sp. gr. 1·4268, at 15·5° C.
,, ,,	,,	,,	,,	...	5 E	,, ,, diluted to sp. gr. 1·1656, at 15·5° C.
,, ,,	,,	,,	,,	63	E	200 c.c. of 5 E nitric acid diluted to 1 litre.
Hydrochloric acid.	HCl	36·5	36·5	...	10 E	Hydrochloric acid, sp. gr. 1·1611, at 15·5° C.
,, ,,	,,	,,	,,	...	5 E	,, ,, diluted to sp. gr. 1·0843, at 15·5° C.
,, ,,	,,	,,	,,	36·5	E	200 c.c. of 5 E hydrochloric acid diluted to 1 litre.
Sulphurous acid.	H_2SO_3	82	41	...	4 E –	Water at 15·5° C., saturated with sulphur dioxide (sp. gr. 1·052).
Carbonic acid.	H_2CO_3	62	31	...	$\frac{E}{10}$ –	Water at 15·5° C., saturated with carbon dioxide.
Acetic acid.	$HC_2H_3O_2$	60	60	...	17 E	Acetic acid solid at 10° C.
,, ,,	,,	,,	,,	...	5 E	294 c.c. of 17 E acetic acid diluted to 1 litre.
,, ,,	,,	,,	,,	60	E	200 c.c. of 5 E ,, ,, ,, ,,
Tartaric acid.	$H_2C_4H_4O_6$	150	75	...	5 E	375 grams dissolved and diluted to 1 litre.
,, ,,	,,	,,	,,	75	E	75 ,, ,, ,, ,,
Citric acid.	$H_3C_6H_5O_7$	192	64	...	5 E	350 ,, ,, ,, ,,
,, ,,	,,	,,	,,	64	E	70 ,, ,, ,, ,,
Oxalic acid.	$H_2C_2O_4$	90	45	...	$\frac{3\ E}{2}$	94·5 ,, ,, ,, ,,
Hydrofluoric acid.	HF	20	20	...	12 E ?	Hydrofluoric acid, sp. gr. 1·15.
Hydrofluosilicic acid.	H_2SiF_6	144	72	...	—	
,, ,,	,,	,,	,,	...	E	
Hydrogen sulphide.	H_2S	34	17	...	$\frac{E}{4}$ –	Water at 15·5° C., saturated with hydrogen sulphide.
Chlorine water.	Cl_2	71	35·5	...	$\frac{E}{5}$ –	Water at 15·5° C., saturated with chlorine.
Bromine.	Br_2	160	80	...	37 E	Pure liquid bromine.
Bromine water.	,,	,,	,,	...	$\frac{E}{2}$	Water at 15·5° C., saturated with bromine.

Hydrogen peroxide.	H_2O_2	34	17	...	4 E –	Hydrogen peroxide, 20 volume solution.
,, ,,	,,	,,	,,	...	2 E –	,, ,, 10 ,, ,,
Potassium hydrate.	KHO	56	56	...	5 E	280 grams, dissolved and diluted to 1 litre.
,, ,,	,,	,,	,,	56	E	56 ,, ,, ,, ,,
Sodium hydrate.	NaHO	40	40	...	5 E	200 ,, ,, ,, ,,
,, ,,	,,	,,	,,	40	E	40 ,, ,, ,, ,,
Ammonium hydrate.	NH_4HO	35	35	...	20 E –	Ammonium hydrate, sp. gr. 0·880.
,, ,,	,,	,,	,,	...	5 E	Ammonium hydrate, diluted to sp. gr. 0·9643 at 15·5° C.
,, ,,	,,	,,	,,	35	E	200 c.c. of 5 E ammonium hydrate, diluted to 1 litre.
Barium oxide.	BaO	153	76·5	...	$\frac{E}{3}$	52·5 grams dissolved and diluted to 1 litre.
Calcium oxide.	CaO	56	28	...	$\frac{E}{20}$	Water at 15·5° C. saturated with calcium hydrate.
Ammonium sulphide.	$(NH_4)_2S$	68	34	...	5 E	Saturate 600 c.c. of 5 E Ammonium hydrate with H_2S in a corked flask, and then add 400 c.c. of 5 E ammonium hydrate.
,, ,,	,,	,,	,,	34	E	200 c.c. of 5 E ammonium sulphide, diluted to 1 litre.
Sodium sulphide.	Na_2S	78	39	...	5 E	Dissolve 200 grams of sodium hydrate in 800 c.c. water, saturate one-half with H_2S, then add the other half and dilute to 1 litre.
,, ,,	,,	,,	,,	39	E	200 c.c. of 5 E sodium sulphide, diluted to 1 litre.
Potassium cyanide.	KCN	65	65	65	E	65 grams crystal, dissolved and diluted to 1 litre.
Potassium sulphate.	K_2SO_4	174	87	87	E	87 grams, dissolved and diluted to 1 litre.
Potassium iodide.	KI	166	166	166	E	166 ,, ,, ,, ,,
,, ,,	,,	,,	,,	—	$\frac{E}{5}$	33·2 ,, ,, ,, ,,
Potassium chromate.	K_2CrO_4	194·5	97·25	97·25	E	97·25 grams disolved and diluted to 1 litre.
Potassium metantimoniate.	$KSbO_3$	209	209	3·07	$\frac{E}{68}$	Saturated solution at 15·5° C.
Potassium ferrocyanide.	$K_4Fe(CN)_6$	368	92	92	E	105·5 grams dissolved and diluted to 1 litre.
Potassium ferricyanide.	$K_6Fe_2(CN)_{12}$	658	109·7	109·7	E	109·7 ,, ,, ,, ,, ,,
Potassium sulphocyanide.	KCNS	97	97	97	E	97 ,, ,, ,, ,, ,,
Sodium carbonate.	Na_2CO_3	106	53	...	3 E	429 ,, ,, ,, ,, ,,
,, ,,	,,	,,	,,	53	E	143 ,, ,, ,, ,, ,,
Hydrogen di-sodium phosphate.	HNa_2PO_4	142	47·3	47·3	$\frac{2E}{3}$ or E	119·3 ,, ,, ,, ,, ,,

REDDROP'S SYSTEM OF CHEMICAL REAGENTS—*continued.*

Name of Reagent.	Symbol.	Molec. Weight.	Equivalent Weight.	Grams per Litre.	Strength.	Method of Preparing Reagent.
Sodium acetate.	$NaC_2H_3O_2$	82	82	...	4 E	544 grams dissolved and diluted to 1 litre.
Sodium sulphite.	Na_2SO_3	126	63	...	2 E–	252 ,, ,, ,, ,, ,,
Sodium thiosulphate.	$Na_2S_2O_3$	158	79	79	$\frac{E}{2}$ or E	124 ,, ,, ,, ,, ,,
Sodium hypochlorite.	NaClO	74·5	74·5	...	...	...
Ammonium acetate.	$(NH_4)C_2H_3O_2$	77	77	...	5 E	294 c.c. of 17 E acetic acid, neutralised with strong ammonium hydrate, and diluted to 1 litre.
,, ,,	,,	,,	,,	77	E	200 c.c. of 5 E ammonium acetate diluted to 1 litre.
Ammonium oxalate.	$(NH_4)_2C_2O_4$	124	62	37·2	$\frac{3\ E}{5}$	42·6 grams dissolved and diluted to 1 litre.
Hydrogen di-ammonium phosphate.	$H(NH_4)_2PO_4$	132	44	44	$\frac{2\ E}{3}$ or E	44 ,, ,, ,, ,, ,,
Ammonium carbonate.	$(NH_4)_2CO_3$	96	48	...	5 E	196·7 grams of ammonium sesquicarbonate dissolved in 333·3 c.c. of 5 E ammonium hydrate and diluted to 1 litre.
,, ,,	,,	,,	,,	48	E	200 c.c. of 5 E ammonium carbonate solution diluted to 1 litre.
Hydrogen ammonium carbonate.	$H(NH_4)CO_3$	79	...	...	$\frac{3\ E}{2}$ or 3E	A saturated solution made by passing excess of carbon dioxide into 3 E ammonium hydrate.
Ammonium chloride.	NH_4Cl	53·5	53·5	...	5 E	267·5 grams dissolved and diluted to 1 litre.
,, ,,	,,	,,	,,	53·5	E	53·5 ,, ,, ,, ,, ,,
Ammonium sulphate.	$(NH_4)_2SO_4$	132	66	66	E	66 ,, ,, ,, ,, ,,
Barium chloride.	$BaCl_2$	208	104	104	E	122 ,, ,, ,, ,, ,,
Barium nitrate.	BaN_2O_6	261	130·5	65·25	$\frac{E}{2}$	65·25 ,, ,, ,, ,, ,,
Barium carbonate.	$BaCO_3$	197	98·5	...	2 E	197 grams freshly precipitated, suspended in water, and diluted to 1 litre.
Strontium sulphate.	$SrSO_4$	183·5	91·75	0·153	$\frac{E}{600}$ –	Water at 15·5° C. saturated with precipitated $SrSO_4$.

Calcium chloride.	$CaCl_2$	111	55·5	55·5	E	109·5 grams dissolved and diluted to 1 litre.
Calcium sulphate.	$CaSO_4$	136	68	2·27	$\frac{E}{30}$	Water at 15·5° C. saturated with precipitated calcium sulphate.
Magnesium chloride.	$MgCl_2$	95	47·5	47·5	E	101·5 grams dissolved and diluted to 1 litre.
Magnesium sulphate.	$MgSO_4$	120	60	60	E	123 ,, ,, ,, ,, ,,
Ferrous sulphate.	$FeSO_4$	152	76	76	E	139 ,, ,, ,, ,, ,,
Ferric chloride.	Fe_2Cl_6	325	54·17	54·17	E	18·67 grams of iron, as $Fe_2H_6O_6$, dissolved in 200 c.c. of 5 E hydrochloric acid, and diluted to 1 litre.
Plumbic acetate.	$PbC_4H_6O_4$	325	162·5	162·5	E	189·5 grams dissolved and diluted to 1 litre.
Plumbic nitrate.	PbN_2O_6	331	165·5	165·5	E	165·5 ,, ,, ,, ,, ,,
Argentic nitrate.	$AgNO_3$	170	170	170	E	170 ,, ,, ,, ,, ,,
,, ,,	,,	,,	,,	...	$\frac{E}{5}$	34 ,, ,, ,, ,, ,,
Argentic sulphate.	Ag_2SO_4	312	156	7·8	$\frac{E}{20}$	Water at 15·5° C. saturated with freshly precipitated argentic sulphate.
Mercurous nitrate.	$Hg_2N_2O_6$	524	262	52·4+	$\frac{E}{5}$+	56 grams dissolved in 40 c.c. of 5 E nitric acid and diluted to 1 litre, a little mercury being placed in the bottle.
Mercuric chloride.	$HgCl_2$	271	135·5	54·2	$\frac{2E}{5}$	54·2 grams dissolved and diluted to 1 litre.
Cupric sulphate.	$CuSO_4$	159·5	79·75	79·75	E	124·75 ,, ,, ,, ,, ,,
Cupric chloride.	$CuCl_2$	134·5	67·25	67·25	E	85·25 ,, ,, ,, ,, ,,
Stannous chloride.	$SnCl_2$	189	94·5	94·5+	E+	112·5 grams dissolved in 200 c.c. of 5 E hydrochloric acid and diluted to 1 litre, a little tin being placed in the bottle.
Auric chloride.	$AuCl_3$	303·1	101	20·2	$\frac{E}{5}$	13·1 grams of metallic gold, converted into auric chloride, dissolved and diluted to 1 litre.
Platinic chloride.	$PtCl_4$	339·1	84·8	84·8	E	49·3 grams of metallic platinum converted into platinic chloride, dissolved and diluted to 1 litre.
Magnesia mixture (for phosphoric acid).	...	...	...	...	E	Dissolve 68 grams $MgCl_2.6H_2O$ in about 500 c.c. of water, add 165 grams NH_4Cl, then 300 c.c. of 5E ammonium hydrate and dilute to one litre.

LIKELY IMPURITIES IN THE ORDINARY REAGENTS.

Reagents.	Impurities.
Sulphuric acid.	Pb, As, Fe, HNO_3, NO_2.
Nitric acid.	H_2SO_4, HCl.
Hydrochloric acid.	Cl, Fe_2Cl_6, H_2SO_4, SO_2, As.
Acetic acid.	H_2SO_4, HCl, Cu, Pb, Fe, Ca.
Oxalic acid.	Fe, K, Na, Ca.
Tartaric acid.	H_2SO_4, Ca.
Sodium hydrate.	Al, SiO_2, phosphates, sulphates, chlorides.
Potassium hydrate.	" " "
Ammonium hydrate.	Sulphate, chloride, carbonates, etc.
Disodium hydrogen phosphate.	Sulphate, chloride, phosphates of alkaline earths.
Sodium acetate.	Sulphates.
Sodium carbonate.	Chloride, phosphates, sulphate, silicates.
Ammonium chloride.	Fe_2Cl_6.
Ammonium carbonate.	Pb, Fe, sulphates and chlorides.
Potassium iodide.	Iodate, carbonate.
Potassium bichromate.	Sulphate.
Calcium chloride.	Fe_2Cl_6.
Cobalt nitrate.	Fe, Ni, etc.
Copper sulphate.	Fe, Zn.
Sulphuretted hydrogen.	This reagent should be used in the gaseous state, and should always be washed before using.

Note.—With the exception of Cl the elements mentioned occur in the combined state.

CHAPTER IV.

NOTES ON THE PRELIMINARY EXAMINATION FOR BASES.

Experiment I.—In heating substances in a glass tube, closed at one end, care should be taken not to start with too high a temperature. Use a low bunsen flame and gradually raise it, noting from stage to stage the changes that take place. If the substance decrepitates—*i.e.*, flies into smaller particles—chlorides, nitrates, etc., may be expected, and should be carefully looked for when testing for acids later on. Test any moisture that is given off with litmus paper to see if it is acid, alkaline or neutral.

When heated at a fairly high temperature, some salts part with their acids and are converted into the oxides of the bases. *Observation* 2 gives the changes in colour of these oxides from hot to cold, by which they can be recognised. *Observation* 3 indicates the presence of salts of the alkalies and alkaline earths, by not changing colour, but by fusing and solidifying when removed from the flame.

If, at a low temperature, fumes are evolved and a sublimate is formed, *i.e.*, a condensation of the volatile substance takes place in the upper or cool part of the tube, Sb_2O_3, NH_4, S, I, Hg, As, may be suspected.

Sb_2O_3 (white fumes) will only rise and settle down in the tube again.

Fumes of NH_4 compounds, Hg and As and some of their compounds, generally rise right up the tube and condense on the cooler part of the tube. S and I also sublime, but can be more easily recognised by their colour—I giving violet vapours condensing to black metallic-looking plates, and S giving yellowish fumes and a yellow sublimate.

As and Hg compounds are reduced by KCN or charcoal to the metallic state and give a black mirror, Hg showing small globules when examined closely, or when the mirror is scraped together with a small splint of wood.

When two or more substances are present together, the reactions of the one may more or less mask the other. Students must be careful not to mistake the darkening of some substances for charring. It is better to make certain by heating strongly some of the original substance on a porcelain dish or crucible lid, when the result can be better seen.

Experiment II. — On charcoal before the blowpipe, chlorides, etc., decrepitate. Chlorates and nitrates, which readily part with some of their oxygen, deflagrate. Salts of the alkalies fuse easily, so are more or less absorbed by the charcoal, and then form fluid beads. The oxides of the alkaline earths, also those of Mg, Zn, Al, Si, etc., are not easily fusible, but remain as white residues, which are highly luminous when heated. Some of these oxides, when heated with $Co(NO_3)_2$, give typical colour reactions, but the oxides of Ba, Sr and Ca remain unchanged, so can be distinguished from the others. Cu, Co, Ni, Fe, Mn, and Cr salts, when heated strongly, leave coloured residues which give typical colour reactions in a borax bead, due to the formation of borates of the metals. If two or more of these metals be present together, the lighter colours will be masked by the darker. Co generally hides the others, and with Ni the blue tint is deeper.

Cr and **Mn**, when fused with Na_2CO_3 and KNO_3, form chromates and manganates of **K** and **Na**, which give the yellow and bluish-green colour to the fused mass.

Experiment III.—On charcoal, with the flux Na_2CO_3 and reducing agents **KCN** and charcoal, some metals are reduced and give beads of the metal, while others give both beads and incrustations. These incrustations are generally the oxides of the metals, formed by the different metals volatilising, and as they pass through the oxidising zone of the flame, they become oxidised and condense on the cooler part of the charcoal. The change of colours of these incrustations from hot to cold corresponds with the changes in the closed tube of the oxides of the different metals. **Fe**, **Ni**, and **Co** are converted into black magnetic oxides. **FeS** may be present in the black mass, being a fusible sulphide.

Experiment IV.—Some chlorides of the metals are volatile and give typical flame reactions; the other salts of these metals do not all give the same reactions, hence there is some difficulty in getting these reactions, especially with some sulphates, *e.g.*, $CaSO_4$.

Experiment V.—NH_3 must be tested for here, as ammonia salts are added to the solutions from time to time in the wet tests, so cannot be tested for there.

Experiment VI.—SiO_2 can generally be detected here by the undissolved residue in the bead, but when fused for some time, some silicates leave no residue, so care must be exercised here. If minerals are to be tested, take a chip in preference to the powdered mineral.

GENERAL TABLE.

Group I. consists of chlorides of **Pb**, **Ag**, and **Hg** (mercurous), precipitated from an aqueous solution by the addition of **HCl**.

The following equations show some of the reactions:—

$$Pb(NO_3)_2 + 2HCl = \underline{PbCl_2} + 2HNO_3$$
$$Pb(C_2H_3O_2)_2 + 2HCl = \underline{PbCl_2} + 2HC_2H_3O_2$$
$$Hg_2(NO_3)_2 + 2HCl = \underline{Hg_2Cl_2} + 2HNO_3$$
$$AgNO_3 + HCl = \underline{AgCl} + HNO_3$$

Group II. consists of sulphides of **Hg**, **Pb**, **Bi**, **Cu**, **Cd**, **Sn**, **Sb**, **As**, etc., precipitated from a dilute **HCl** solution by passing H_2S gas slowly through the solution to saturation.

The following equations show the reactions:—

$$HgCl_2 + H_2S = \underline{HgS} + 2HCl$$
$$PbCl_2 + H_2S = \underline{PbS} + 2HCl$$
$$2BiCl_3 + 3H_2S = \underline{Bi_2S_3} + 6HCl$$
$$CuCl_2 + H_2S = \underline{CuS} + 2HCl$$
$$CdCl_2 + H_2S = \underline{CdS} + 2HCl$$
$$SnCl_2 + H_2S = \underline{SnS} + 2HCl$$
$$SnCl_4 + 2H_2S = \underline{SnS_2} + 4HCl$$
$$2SbCl_3 + 3H_2S = \underline{Sb_2S_3} + 6HCl$$
$$2SbCl_5 + 5H_2S = \underline{Sb_2S_5} + 10HCl$$
$$2AsCl_3 + 3H_2S = \underline{As_2S_3} + 6HCl$$

After the precipitation of Group II., it is necessary to rid the filtrate of

Note.—Formulæ underlined represent precipitates. The arrow sign (⟶) represents a volatile substance.

the excess of H_2S by boiling. H_2S being a reducing agent, reduces any ferric salts that may be in solution to ferrous salts, and before proceeding to precipitate Group III*a*, it is necessary to reconvert them back to the ferric form in order to completely precipitate them with NH_4OH; therefore, after getting rid of the reducing agent, HNO_3 is added to assist oxidation.

$$3FeCl_2 + 3HCl + HNO_3 = 3FeCl_3 + NO + 2H_2O$$

Before precipitating Group III*a*, the solution is tested for H_3PO_4, as NH_4OH precipitates the phosphates of Groups III*b*, IV., and of **Mg**.

The precipitate formed on the addition of $(NH_4)_2MoO_4$ is believed to have the composition $12MoO_3$, $(NH_4)_3PO_4$.

Group IIIa.—In the presence of NH_4Cl the hydroxides of **Mn, Zn, Ni, Co,** and **Mg** are not precipitated by NH_4OH, owing to the formation of soluble double chlorides. (For example, see Group V.)

The following equations show the reactions with NH_4OH:—

$$Fe_2Cl_6 + 6NH_4OH = \underline{Fe_2(OH)_6} + 6NH_4Cl$$
$$Cr_2Cl_6 + 6NH_4OH = \underline{Cr_2(OH)_6} + 6NH_4Cl$$
$$Al_2Cl_6 + 6NH_4OH = \underline{Al_2(OH)_6} + 6NH_4Cl$$

Group IIIb consists of the sulphides of **Zn, Mn, Ni,** and **Co** precipated from an ammoniacal solution by passing H_2S gas slowly through it to saturation.

The following equations show the reactions:—

$$ZnCl_2 + (NH_4)_2S = \underline{ZnS} + 2NH_4Cl$$
$$MnCl_2 + (NH_4)_2S = \underline{MnS} + 2NH_4Cl$$
$$NiCl_2 + (NH_4)_2S = \underline{NiS} + 2NH_4Cl$$
$$CoCl_2 + (NH_4)_2S = \underline{CoS} + 2NH_4Cl$$

Group IIIc consists of hydrates of **Fe, Al,** and **Cr,** also phosphates of **Fe, Cr, Al, Zn, Mn, Ni, Co, Ba, Sr, Ca,** and **Mg.** All these phosphates are soluble in **HCl,** but are precipitated by the addition of solutions of the alkalies, such as NH_4OH, **KOH,** and **NaOH.** For example—

$$\underline{Ca_3(PO_4)_2} + 6HCl = 3CaCl_2 + 2H_3PO_4$$
$$\underline{BaHPO_4} + 2HCl = BaCl_2 + H_3PO_4$$
$$3CaCl_2 + 2H_3PO_4 + 6NH_4OH = \underline{Ca_3(PO_4)_2} + 6NH_4Cl + 6H_2O$$
$$BaCl_2 + H_3PO_4 + 2NaOH = \underline{BaHPO_4} + 2NaCl + 2H_2O$$

Group IV. consists of the carbonates of **Ba, Sr,** and **Ca,** precipitated from an ammoniacal solution by $(NH_4)_2CO_3$.

The following equations show the reactions—

$$BaCl_2 + (NH_4)_2CO_3 = \underline{BaCO_3} + 2NH_4Cl$$
$$SrCl_2 + (NH_4)_2CO_3 = \underline{SrCO_3} + 2NH_4Cl$$
$$CaCl_2 + (NH_4)_2CO_3 = \underline{CaCO_3} + 2NH_4Cl$$

Group V.—**Mg** is precipitated as phosphate by the addition of Na_2HPO_4 to the ammoniacal solution.

Group IIIa.
$$MgCl_2 + 2NH_4OH = \underline{Mg(OH)_2} + 2NH_4Cl$$
$$Mg(OH)_2 + 4NH_4Cl = 2NH_4OH + MgCl_2,\ 2NH_4Cl$$

Group V.—$MgCl_2,\ 2NH_4Cl + 2NH_4OH + Na_2HPO_4 = \underline{NH_4MgPO_4}$
$$+ 2NH_4Cl + 2NaCl + NH_4OH + H_2O$$

NH_4MgPO_4 is appreciably soluble in H_2O but insoluble in NH_4OH.

K is precipitated, after driving off the ammonium salts, by $PtCl_4$. K_2PtCl_6 being soluble in H_2O and the alkalies but insoluble in alcohol, the latter is added to completely precipitate it.

$$2KCl + PtCl_4 = \underline{K_2PtCl_6}$$

REACTIONS IN GROUP I.

In this group Ag, Pb, and Hg (mercurous) are thrown down as chlorides, advantage being taken of the insolubility of these chlorides in cold water solutions.

$PbCl_2$ being soluble in boiling water, is separated from the other two by treating the mixed precipitates of the three bases with boiling water and filtering the solution quickly, then allowing it to cool, when the $PbCl_2$ comes down again in acicular crystals.

AgCl is insoluble in hot water but readily soluble in NH_4OH.

$$\underline{2AgCl} + 3NH_4OH = 2AgCl.3NH_3 + 3H_2O$$

This compound ($2AgCl.3NH_3$) is decomposed by HNO_3

$$2AgCl.3NH_3 + 3HNO_3 = \underline{2AgCl} + 3NH_4NO_3$$

Hg_2Cl_2 by the action of NH_4OH is converted into the black mercurous ammonium chloride.

$$\underline{Hg_2Cl_2} + 2NH_4OH = \underline{NH_2Hg_2Cl} + NH_4Cl + 2H_2O$$

This mercurous compound, in the presence of AgCl and excess of NH_4OH, passes into the corresponding and more stable mercuric salt, NH_2HgCl, and the mercury it loses reduces a portion of the AgCl.

$$\underline{Hg_2Cl_2} + \underline{2AgCl} + 4NH_4OH = \underline{2NH_2HgCl} + 2NH_4Cl + 4H_2O + \underline{2Ag}$$

In this separation a small quantity of silver, in the presence of a large amount of mercury, might not be detected, being entirely precipitated with the mercury compound.

REACTIONS IN GROUP II.

In this group certain of the sulphides are soluble in $(NH_4)_2S$, also in KOH and NaOH, which affords an opportunity of dividing it into two divisions. Division I. contains the sulphides of As, Sb, and Sn (Au and Pt) soluble in $(NH_4)_2S$, KOH, and NaOH.

$$\underline{As_2S_3} + 3(NH_4)_2S = 2(NH_4)_3AsS_3$$
$$\underline{As_2S_3} + 6KOH = K_3AsO_3 + K_3AsS_3 + 3H_2O$$
$$\underline{As_2S_3} + 6NaOH = Na_3AsO_3 + Na_3AsS_3 + 3H_2O$$

Sb_2S_3 (antimonious sulphide) gives the same reaction with $(NH_4)_2S$ as As_2S_3, but the following with KOH and NaOH,

$$\underset{\text{(Na)}}{\underline{2Sb_2S_3}} + 4KOH = \underset{\text{(Na)}}{3KSbS_2} + \underset{\text{(Na)}}{KSbO_2} + 2H_2O$$

Sb_2S_5 (antimonic sulphide) gives the following reactions with KOH:—

$$\underline{4Sb_2S_5} + 18KOH = 5K_3SbS_4 + 3KSbO_3 + 9H_2O$$

SnS (stannous sulphide) gives the following reaction with KOH:—

$$\underline{2SnS} + 4KHO = K_2SnO_2 + K_2SnS_2 + 2H_2O$$

SnS_2 (stannic sulphide) with $(NH_4)_2S$ and KOH.

$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3$$
$$3SnS_2 + 6KHO = 2K_2SnS_3 + K_2SnO_3 + 3H_2O$$

NaOH reacts in a similar manner to KOH with these sulphides.

From these alkaline solutions the sulphides are thrown down unchanged by dilute HCl.

$$K_3AsO_3 + K_3AsS_3 + 6HCl = As_2S_3 + 6KCl + 3H_2O$$
$$3KSbS_2 + KSbO_2 + 4HCl = 2Sb_2S_3 + 4KCl + 2H_2O$$
$$5K_3SbS_4 + 3KSbO_3 + 18HCl = 4Sb_2S_5 + 18KCl + 9H_2O$$
$$K_2SnO_2 + K_2SnS_2 + 4HCl = 2SnS + 4KCl + 2H_2O$$
$$2K_2SnS_3 + K_2SnO_3 + 6HCl = 3SnS_2 + 6KCl + 3H_2O$$

These sulphides are then treated with strong HCl; As_2S_3 is not acted upon, but the sulphides of Sn and Sb are decomposed.

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S\rightarrow$$
$$Sb_2S_5 + 10HCl = 2SbCl_5 + 5H_2S\rightarrow$$
$$SnS + 2HCl = SnCl_2 + H_2S\rightarrow$$
$$SnS_2 + 4HCl = SnCl_4 + 2H_2S\rightarrow$$

These chlorides are filtered off, diluted, and a piece of Zn foil and Pt foil are placed in contact in the solution, when the Sb is deposited on the Pt foil by galvanic action and the Sn on the Zn foil. The Sb is dissolved off the Pt with HNO_3, and then precipated by H_2S gas being passed through the solution, and Sn is dissolved in as little hot HCl as possible, and $HgCl_2$ is added to this solution.

$$SnCl_2 + 2HgCl_2 = SnCl_4 + 2HgCl$$

Division II. contains the sulphides of Hg, Pb, Bi, Cd and Cu, which are decomposed with HNO_3, with the exception of HgS; this only upon prolonged boiling is partially converted into the nitrate. PbS may be partly oxidised into $PbSO_4$.

$$PbS + 2NHO_3 = Pb(NO_3)_2 + H_2S\rightarrow$$
$$Bi_2S_3 + 6HNO_3 = 2Bi(NO_3)_3 + 3H_2S\rightarrow$$
$$CdS + 2HNO_3 = Cd(NO_3)_2 + H_2S\rightarrow$$
$$CuS + 2HNO_3 = Cu(NO_3)_2 + H_2S\rightarrow$$

HgS is dissolved in aqua regia, then diluted, and a strip of Cu placed in the solution.

$$HgCl_2 + Cu = CuCl_2 + Hg$$

Pb is precipitated by H_2SO_4, alcohol being added to completely precipitate it as $PbSO_4$.

$$Pb(NO_3)_2 + H_2SO_4 = PbSO_4 + 2HNO_3$$

Bi is precipitated by NH_4OH.

$$2Bi(NO_3)_3 + 6NH_4OH = Bi_2(HO)_6 + 6NH_4NO_3$$
$$Bi_2(HO)_6 + 6HCl = 2BiCl_3 + 6H_2O$$
$$BiCl_3 + H_2O = BiOCl + 2HCl$$

Cd is precipitated from the ammoniacal solution by passing H_2S gas through it.

$$Cd(NO_3)_2 + 2NH_4OH = Cd(OH)_2 + 2NH_4NO_3$$

$Cd(OH)_2$ is soluble in the excess of NH_4OH.

$$Cd(OH)_2 + H_2S = CdS + 2H_2O$$

Cu gives a deep blue solution with excess of NH_4OH.

$$Cu(NO_3)_2 + 4NH_4OH = Cu(NO_3)_2, 4NH_3, H_2O + 3H_2O$$

This blue solution is decolorised by the addition of KCN, when the Cu is converted into a double cyanide, having the formula $2KCN.Cu(CN)_2$, which passes quickly into the cuprous form, $Cu_2(CN)_2.6KCN$. CuS is not precipitated by H_2S when there is an excess of KCu in solution, hence Cd can be separated. $K_4Fe(CN)_6$ precipitates cupric ferrocyanide, $Cu_2Fe(CN)_6$, insoluble in acids, but decomposed by alkalis, so the solution is made acid with CH_3COOH before adding $K_4Fe(CN)_6$.

REACTIONS OF GROUP IIIa.

In this group the hydroxides of Al, Fe and Cr are dissolved in HCl.

$$\underline{Al_2(HO)_6} + 6HCl = Al_2Cl_6 + 6H_2O$$
$$\underline{Cr_2(HO)_6} + 6HCl = Cr_2Cl_6 + 6H_2O$$
$$\underline{Fe_2(HO)_6} + 6HCl = Fe_2Cl_6 + 6H_2O$$

KOH and NaOH produce the same precipitate as NH_4OH, only the hydroxides of Al and Cr are readily soluble in excess of these reagents.

$$\underline{Al_2(OH)_6} + 6NaOH = Al_2O_3.3Na_2O + 6H_2O$$
$$\underline{Cr_2(OH)_6} + 2KOH = Cr_2O_3.K_2O + 4H_2O$$

$Cr_2(HO)_6$ can be precipitated by boiling, while the sodium aluminate remains in solution.

The hydroxides of Cr and Fe are dried and then fused with Na_2CO_3 and KNO_3.

$$\underline{Cr_2O_3} + \underline{2Na_2CO_3} + O_3 = \underline{2Na_2CrO_4} + 2CO_2$$

The Fe_2O_3 remains unchanged.

Na_2CrO_4 is dissolved out with water, and CH_3COOH and $Pb(C_2H_3O_2)_2$ added to the solution.

$$Na_2CrO_4 + Pb(C_2H_3O_2)_2 = \underline{PbCrO_4} + 2NaC_2H_3O_2$$

Fe_2O_3 is dissolved in HCl, and $K_4Fe(CN)_6$ added to the solution.

$$2Fe_2Cl_6 + 3K_4Fe(CN)_6 = Fe_4(Fe(CN)_6)_3 + 12KCl$$

$Al_2O_3.3NaO$ is decomposed with HCl, and the Al is precipitated as hydroxide with NH_4OH.

$$Al_2O_3.3Na_2O + 12HCl = Al_2Cl_6 + 6NaCl + 6H_2O$$
$$Al_2Cl_6 + 6NH_4OH = Al_2(OH)_6 + 6NH_4Cl$$

REACTIONS OF GROUP IIIb.

In this group the sulphides of Zn, Mn, Ni and Co are decomposed with HCl, using a crystal or two of $KClO_3$ when the latter two sulphides are present.

$$\underline{ZnS} + 2HCl = ZnCl_2 + H_2S \rightarrow$$
$$\underline{MnS} + 2HCl = MnCl_2 + H_2S \rightarrow$$

The hydroxides of Mn, Ni, and Co are precipitated by the addition of NaOH or KOH; but the hydroxide of Zn is soluble in excess of either of these reagents.

$$\underline{Zn(OH)_2} + 2NaOH = ZnNa_2O_2 + 2H_2O$$
$$MnCl_2 + 2NaOH = \underline{Mn(OH)_2} + 2NaCl$$
$$NiCl_2 + 2NaOH = \underline{Ni(OH)_2} + 2NaCl$$
$$CoCl_2 + 2NaOH = \underline{Co(OH)_2} + 2NaCl$$

The solution containing the $ZnNa_2O_2$ is filtered, and the Zn is precipitated by passing H_2S gas through it.

$$ZnNa_2O_2 + 2H_2S = \underline{ZnS} + Na_2S + 2H_2O$$

The hydrates of Mn, Ni and Co are then converted into chlorides by treating them with dilute HCl. The solution is nearly neutralised with NH_4OH, and an excess of $(NH_4)C_2H_3O_2$ is added, which converts the $MnCl_2$ into the acetate, from which solution MnS is not precipitated by passing H_2S gas.

$$MnCl_2 + 2(NH_4)C_2H_3O_2 = Mn(C_2H_3O_2)_2 + 2NH_4Cl$$

The solution of $Mn(C_2H_3O_2)_2$ is then filtered off from sulphides of Ni and Co, and the Mn is precipitated as carbonate by the addition of Na_2CO_3.

$$Mn(C_2H_3O_2)_2 + Na_2CO_3 = \underline{MnCO_3} + 2NaC_2H_3O_2.$$

The NiS and CoS are converted into chlorides by treating with HCl and $KClO_3$; Cl is boiled off, and the excess of acid is neutralised by the addition of Na_2CO_3. An excess of KCN solution is then added, forming double cyanides of Ni and Co.

$$NiCl_2 + 4KCN = 2KCN.Ni(CN)_2 + 2KCl$$
$$CoCl_2 + 6KCN = 4KCN.Co(CN)_2 + 2KCl$$

To the solution containing the double cyanides is added an excess of NaOH and then Br water, which precipitates the Ni as the hydrated sesquioxide and oxidises the potassium cobalto-cyanide into the potassium cobalti-cyanide.

$$2K_2Ni(CN)_4 + 2NaOH + Br_2 + 4H_2O = \underline{Ni_2(OH)_6} + 4KCN + 2NaBr + 4HCN$$
$$2K_4Co(CN)_6 + 2NaOH + Br_2 = 2K_3Co(\underline{CN)_6} + 2KOH + 2NaBr.$$

REACTIONS OF GROUP IIIc.

In this group the phosphates and hydrates are dissolved in HCl and the excess of acid is neutralised with Na_2CO_3, then a solution of $NaC_2H_3O_2$ and CH_3COOH is added. Al, Cr, and Fe are precipitated as phosphates.

$$\left.\begin{matrix} Fe_2Cl_6 \\ Al_2Cl_6 \\ Cr_2Cl_6 \end{matrix}\right\} + 2H_3PO_4 = 2M'''PO_4 + 6HCl$$

If there is excess of H_3PO_4 in solution, or none of the above bases are present, then Fe_2Cl_6 is added, drop by drop, as long as a precipitate falls; when a yellow colour appears, ferric acetate is being formed, in which ferric phosphate is soluble, therefore care must be taken only to add sufficient Fe_2Cl_6 to precipitate the H_3PO_4 in solution. All the phosphoric acid being removed, chlorides of Groups III. and IV. only remain, and are treated as in the General Table.

REACTIONS OF GROUP IV.

In this group the carbonates of Ba, Sr and Ca are decomposed with HCl, and the solution is divided into two portions:—

1*st portion*—$CaSO_4$ solution is added to test for presence of Ba.

$$BaCl_2 + CaSO_4 = \underline{BaSO_4} + CaCl_2.$$

2nd portion.—NH_4OH is added to neutralise excess of HCl, and then CH_3COOH in excess is added to convert to acetates.

$$\left.\begin{matrix}BaCl_2\\SrCl_2\\CaCl_2\end{matrix}\right\} + 2CH_3COOH = M''(C_2H_3O_2)_2 + 2HCl$$

From the solution of acetates, $K_2Cr_2O_7$ throws down $BaCrO_4$.

$$2Ba(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O = \underline{2BaCrO_4} + 2KC_2H_3O_2 + 2CH_3COOH.$$

Sr is then thrown down by the addition of K_2SO_4.

$$Sr(C_2H_3O_2)_2 + K_2SO_4 = \underline{SrSO_4} + 2KC_2H_3O_2.$$

To the remaining solution an excess of NH_4OH is added and $(NH_4)_2C_2O_4$, when the **Ca** is precipitated as oxalate.

$$Ca(C_2H_3O_2)_2 + (NH_4)_2C_2O_4 = \underline{CaC_2O_4} + 2(NH_4)C_2H_3O_2$$

PART II.

CHAPTER I.

THE SPECTROSCOPE FOR QUALITATIVE ANALYSIS.

Fig. 35 gives the student an idea of the spectroscope and of its different parts.

P is a flint glass prism, having a refracting angle of 60° and resting on a brass plate fixed on a brass support, S. The brass plate carries the collimator tube C, in the end of which nearest to the prism is fixed a lens, the other end being closed by a plate in which there is a vertical slit, which can be widened or narrowed as required by means of a small screw.

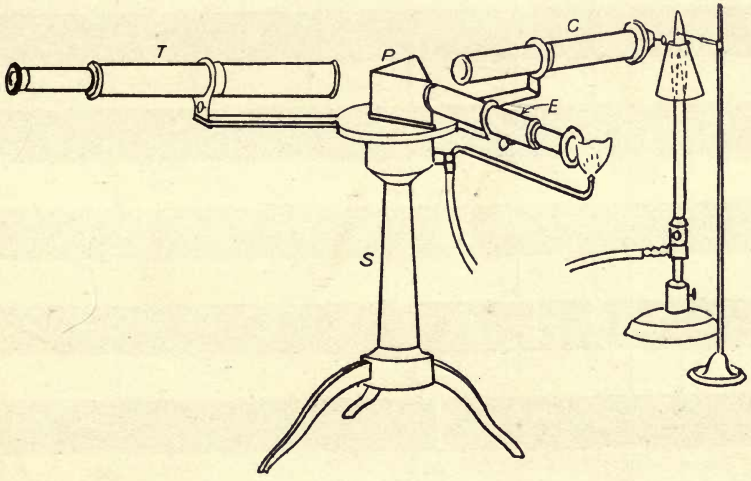


Fig. 35.

The tube E has also on the end nearest the prism a lens, and at the other end a reduced photographic millimetre scale which can be seen through the telescope T. At the end of E is placed an ordinary gas burner, a little distance from the photographic scale. Right opposite the slit in the collimator tube C is placed an ordinary bunsen flame, in which the substance to be tested is placed in the loop of a platinum wire. E is adjusted so that the image of the illuminated scale can be seen through

the telescope T, and the divisions are focussed by means of a small screw on E. All extraneous rays of light are shut off by covering up the apparatus with a black cloth or experimenting in a dark room.

Fig. 36 gives the spectra of the alkalis and alkaline earths, and with

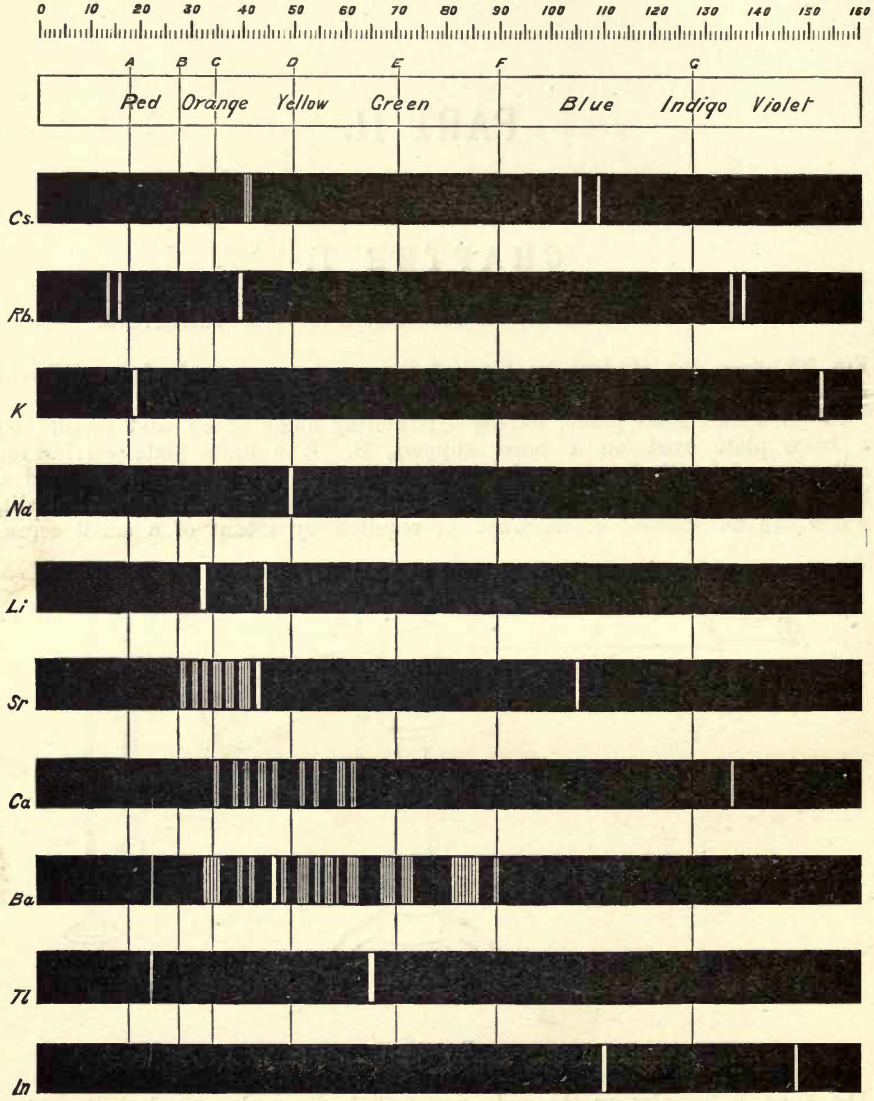


FIG. 36.

care in adjusting the spectroscope a good many of these lines can be seen.

The chlorides of these metals are used for the analysis, but in the case of potassium the solid KNO_3 is recommended to be used in the Pt. loop, as this brings out the violet line more distinctly.

The student should take all these salts in the order given, and in his note-book draw to scale each spectrum, only putting in the lines observed, then compare them with the chart.

TESTS FOR SOME OF THE RARER METALS.

Thallium.—Soluble in HNO_3. Tl_2O is very soluble in H_2O. HCl (conc.) precipitates TlCl (ous), white p'p't, from aqueous solutions, slightly soluble in H_2O, insoluble in NH_4OH, but soluble in H_2SO_4.

H_2S gives no p'p't from mineral acid solutions, but from an acetic acid solution a brown p'p't of Tl_2S is thrown down. $(NH_4)_2S$ also p'p'tes Tl_2S.

$PtCl_4$ p'p'tes from solutions of thallous salts, a yellow p'p't of Tl_2PtCl_6.

Tungsten.—Insoluble in HCl or H_2SO_4, slowly soluble in HNO_3 or aqua regia. Mineral generally fused with Na_2CO_3 and $NaNO_3$, when tungstates of the alkalis are formed which are soluble in H_2O.

HCl in excess in an aqueous solution cold, gives a white p'p't of $H_2WO_4.H_2O$; hot, a yellow p'p't of H_2WO_4.

H_2S gives no p'p't in acid solutions, but turns the solution a blue colour. A solution of a tungstate with Zn, Sn, or $SnCl_2$, and an excess of HCl, gives a characteristic blue colour.

Gold and Platinum are insoluble in HCl, HNO_3, or H_2SO_4, but soluble in aqua regia, yielding chlorides $AuCl_3$ and $PtCl_4$.

H_2S gives black p'p'tes of AuS and PtS_2 from chloride solutions in the cold, insoluble in HCl or HNO_3, but soluble in aqua regia and $(NH_4)_2S$. (PtS_2 is only partially dissolved in $(NH_4)_2S$ in the presence of other sulphides.) In boiling solutions metallic Au is p'p'ted and not AuS. From the $(NH_4)_2S$ solution, AuS and PtS_2 are p'p'ted by the addition of HCl.

$FeSO_4$ gives a brownish p'p't of metallic Au with $AuCl_3$ solution. If $AuCl_3$ solution is weak, a bluish coloration only is seen. Pt is p'p'ted by $FeSO_4$ only after boiling for some time.

$SnCl_2$ gives a purple p'p't (purple of cassius) in dilute solutions of $AuCl_3$.

NH_4Cl with $AuCl_3$ and $PtCl_4$ forms chloroaurates and chloroplatinates (NH_4AuCl_4 and $(NH_4)_2PtCl_6$).

$C_2H_2O_4$ p'p'tes Au but not Pt from chloride solutions.

To solution of $AuCl_3 + PtCl_4$ add $C_2H_2O_4$

P'p't = Au.	Solution.—Evaporate down with NH_4Cl = yellow p'pt $(NH_4)_2PtCl_6$.

Rhodium.—Alloyed with other metals Rh is soluble in aqua regia.

H_2S.—From a hot solution of its salts, p'p'tes a sulphide insoluble in alkali sulphides.

Fused with $KHSO_4$, and the fused mass treated with H_2O, a pink solution is obtained. Fused with KOH and KNO_3 gives RhO_2, insoluble in acids and alkalis.

Melted with Zn and the alloy boiled with an acid, Rh is left as a black powder.

Palladium.—*Slowly soluble* in HCl or H_2SO_4; dissolves in the cold in HNO_3, forming Pd $(NO_3)_2$. *Soluble* in aqua regia, forming $PdCl_4$.

H_2S p'p'tes it as PdS, insoluble in $(NH_4)_2S$. $PdCl_4$ is very unstable,

and is decomposed, even in solution, into $PdCl_2$ and free Cl. KI p'p'tes black PdI_2.

Pd salts are easily reduced to metal Pd either by heat or by the action of reducing agents.

Osmium.—The metal in compact form is not attacked by acids. The p'p'ted metal is slowly dissolved by aqua regia or fuming HNO_3. In alloys treated with aqua regia, and the residue heated in a porcelain tube through which air is passed, OsO_4 (perosmic anhydride) is given off; a peculiar and irritating vapour, poisonous and injurious to the eyes. OsO_4 is soluble in H_2O, giving a neutral solution with powerful oxidising properties; bleaches indigo and liberates I from KI. Mixed with KCl and heated in Cl, the mass then treated with H_2O and evaporated, red crystals of $2KCl,OsCl_4$ separate. H_2S gives a brownish black p'p't, OsS, in strongly acid solutions insoluble in $(NH_4)_2S$.

Iridium.—Insoluble in acids and aqua regia. Freshly p'p'ted it is soluble in aqua regia. Mixed with NaCl and heated in a current of Cl, Na_2IrCl_6 is formed, soluble in boiling water. H_2S reduces $IrCl_4$ to Ir_2Cl_6 and p'p'tes Ir_2S_3 as a brown p'p't, soluble in excess of $(NH_4)_2S$.

NH_4Cl p'p'tes $(NH_4)_2IrCl_6$ a dark red-brown p'p't which upon ignition leaves metallic Ir.

Tellurium. — Insoluble in HCl; soluble in HNO_3 and aqua regia. H_2SO_4 (conc.) produces a purplish-red solution on cooling.

Fused with Na_2CO_3 on charcoal it forms Na_2Te, which is decomposed with acids forming H_2Te, a gas of very disagreeable odour.

H_2S p'p'tes a brown sulphide soluble in $(NH_4)_2S$.

TeO_2 dissolves in KOH and NaOH, forming tellurites.

Selenium.—Soluble in HNO_3 and aqua regia. H_2SO_4 (conc.) gives a green coloured solution on cooling, from which solution H_2O p'p'tes it as a red powder. Fused with Na_2CO_3 on charcoal it forms Na_2Se, which is decomposed with HCl and forms H_2Se, a gas smelling of putrid horse-radish.

H_2S p't'tes Se and S from selenious compounds, a lemon yellow p'p't which becomes red on heating.

SeO_2 is soluble in H_2O.

Molybdenum. — Insoluble in HCl and dilute H_2SO_4 converted into molybdic acid by HNO_3.

MoO_3 is soluble in strong NH_4OH forming NH_4HMoO_4.

HNO_3 and HCl p'p't H_2MoO_4 from concentrated molybdate solutions.

H_2S from acid solutions, p'p'tes MoS_3, a brownish-black p'p't soluble in $(NH_4)_2S$.

$(NH_4)_2MoO_4$ used for testing for H_3PO_4 (see General Table).

Beryllium or **Glucinum.**—Occurs generally as silicate with Al_2O_3 (beryl) or with Al_2O_3 (chrysoberyl). Mineral; fuse with four times its weight of $(NaK)Co_3$, decompose fused mass with HCl and evaporate to dryness to separate SiO_2. Take up with HCl, filter, and to the solution add excess of $(NH_4)_2CO_3$, $Al_2(OH)_6$ is p'p'ted. $Be(OH)_2$ is soluble in the excess of $(NH_4)_2CO_3$. Acidify solution with HCl and add NH_4OH; $Be(OH)_2$ is thrown down. BeO_2 is soluble in acids.

Salts of Be have a sweetish taste.

Zirconium.—Occurs chiefly as silicate, $ZrSiO_4$ (zircon). Mineral. Heat with KHF_2 and boil with H_2O; K_2ZrF_6 is dissolved; heat solution with H_2SO_4 to expel HF, and then p'p'te Zr with NH_4OH as $ZrO(OH)_2$.

$ZrO(OH)_2$ is insoluble in excess of NaOH and KOH.

$C_2H_2O_4$ p'p'tes Zr as oxalate, soluble in excess of $(NH_4)_2C_2O_4$.

Thorium.—Occurs chiefly as silicate (thorite). H_2SO_4 decomposes the mineral, and the sulphate of Th can be p'p'ted by boiling. $C_2H_2O_4$ p'p'tes a white oxalate of Th, insoluble in dilute acids, soluble in $NH_4C_2H_3O_2 + CH_3COOH$.

ThO_2 can be obtained by igniting the oxalate.

Yttrium.—Occurs in rare minerals, such as Gadolinite, Orthite, etc.

Can be dissolved out by acids.

Yttrium salts are white.

NH_4OH p'p'tes the hydrate insoluble in excess.

$C_2H_2O_4$ p'p'tes the white oxalate of Y, insoluble in excess, partially dissolved by boiling with $(NH_4)_2C_2O_4$.

Titanium.—Occurs generally as TiO_2 in minerals, such as Ilmenite, Rutile, Anatase, etc. The mineral is fused with $KHSO_4$, the fused mass is then treated with cold water and filtered. H_2SO_3 is added to the filtrate and it is boiled, when H_2TiO_3 separates out as a white p'p't.

An acid solution of TiO_2, when treated with Zn or Sn, gives a violet or light-blue colour to the solution.

Uranium.—Occurs in nature in the minerals Pitchblende, Uranite, etc.

UO_2 (ous), brown or black, dissolves in HNO_3 and forms uranic nitrate $(UO_2(NO_3)_2)$.

UO_3 (ic), brick red, dissolves in HCl.

Uranic salts (yellow colour) in H_2SO_4 solution, warmed with Zn, change colour of solution to a green colour; $(NH_4)_2S$ from cold neutral solutions, in presence of NH_4Cl, throws down a chocolate-brown p'p't soluble in acids, including CH_3COOH.

Lithium.—Occurs in mineral waters as Li_2CO_3, and in some minerals as silicate, such as Lepidolite, etc. Most of the lithium salts are soluble in water, the carbonate, hydroxide, and phosphate being less soluble than the others.

The chloride and nitrate are soluble in a mixture of alcohol and ether, which distinguish it from Na and K.

Na_2HPO_4 p'p'tes Li_3PO_4 as a white p'p't on boiling. P'p'tion more complete in the presence of NaOH.

Li salts impart a deep carmine colour to the flame.

Spectrum—one red and one orange line.

MINERALS AND ALLOYS FOR QUALITATIVE ANALYSIS.

Minerals.—Calcite, dolomite, magnesite, siderite, apatite, fluorite, barytes, celestine, felspar, galena, blende, iron and copper pyrites, stibnite, smaltine, fahl ores, bismuthinite, calaverite, chromite, wolfram, topaz, beryl, tourmaline.

Alloys.—Brass, Muntz metal, bell metal, Britannia metal, soft solder, phosphor bronze, rose metal, aluminium bronze, German silver, steel.

At least six of the above minerals and four of the alloys are recommended to be analysed by each student, and should be selected by the demonstrator.

Before proceeding to the analysis of minerals and alloys the student should be thoroughly conversant with all the qualitative tables and should be able to apply them without any difficulty. Too much importance cannot be placed on the preliminary tests, as most of the bases should be detected there first and afterwards confirmed in the wet way.

A careful qualitative analysis should always be made of a substance before the quantitative is begun, as the methods to be adopted in the latter greatly depend upon what is present.

SOLUBILITY TABLE.

V.S. = very soluble. S. = soluble. Sp.S. = sparingly soluble. Ins. = insoluble. Alcohol = absolute Ethyl.

* These terms are approximate, and are intended as a guide to the choice of solvent. For greater accuracy consult Comey's *Dictionary of Chemical Solubilities*.

Substance.	Formula.	Water.	Acids.	Alcohol.
Acetate of aluminium	$Al_2C_{12}H_{18}O_{12}$	V.S.	...	...
,, ammonium	$(NH_4)C_2H_3O_2$	V.S.	...	S.
,, antimony	$SbC_6H_9O_6$	S.	...	S.
,, barium	$BaC_4H_6O_4Aq$	V.S.	...	Sp.S.
,, bismuth	$BiC_6H_9O_6$	S.	...	...
,, cadmium	$CdC_4H_6O_4.3Aq$	V.S.	...	...
,, calcium	$CaC_4H_6O_4+Aq$	V.S.	...	Sp.S.
,, chromium	$Cr_2C_{12}H_{18}O_{12}$	S.	...	Ins.
,, cobalt (ous)	$CoC_4H_6O_4.4Aq$	V.S.	...	...
,, ,, (ic)	...	S. decomposed by boiling	...	...
,, copper (ous)	$Cu_2C_3H_6O_4$	Decomposed	...	Sp.S.
,, ,, (ic)	$CuC_4H_6O_4.Aq$	S. to V.S.	S.	Sp.S.
,, iron(ic) (Basic)	$Fe_2C_8H_{12}O_8(OH)_2$	S.	S.	S.
,, lead	$PbC_4H_6O_4.3Aq$	V.S.	...	Sp.S.
,, lithium	$LiC_2H_3O_2.2Aq$	V.S.	...	V.S.
,, magnesium	$MgC_4H_6O_4.4Aq$	V.S.	...	V.S.
,, manganese	$MnC_4H_6O_4.4Aq$	V.S.	...	S.
,, mercury (ous)	$Hg_2C_4H_6O_4$	Sp.S.	...	Sp.S.
,, ,, (ic)	$HgC_4H_6O_4$	S.	...	Decomposed
,, nickel	$NiC_4H_6O_4.5Aq$	V.S.	...	Ins.
,, potassium	$KC_2H_3O_2$	V.S.	S. CH_3COOH	V.S.
,, silver	$AgC_2H_3O_2$	Sp.S. to S.	...	...
,, sodium	$NaC_2H_3O_2.3Aq$	V.S.	...	V.S.
,, strontium	$SrC_4H_6O_4+xAq$	V.S.	...	S.
,, tin (ous)	$SnC_4H_6O_4$	S.	...	Ins.
,, ,, (ic)	$SnC_8H_{12}O_8$	S.	...	...
,, zinc	$ZnC_4H_6O_4.3Aq$	V.S.	...	S.
Alums	...	S. to V.S.	...	...
Aluminates	...	Insol. except Na, K, Ba, S, Aq	Sp.S. to S.	...
Antimoniates	M'_3SbO_4 and $M'SbO_3$	Nearly all Ins. or V. Sp.S.	...	Almost Ins.
Arsenites and arsenates	$M'AsO_2$ ... M'_3AsO_4 ...	Those of the alkalis are S.; most others Ins.	S.	...
Benzoates	...	Nearly all S—a few Sp.S.	S.	...
Boric acid	H_3BO_3	S. to V.S.	...	S.
Borates	...	Those of the alkalis are S.—the rest dif. S.	S. H_3BO_3 HNO_3, &c.	Ins. or nearly so
Bromates	$M'BrO_3$ ...	Mostly V.S. Hg (ous); Ag Sp.S.	...	Mostly Ins. to Sp.S.
Bromine	Br_2	S. in 33·3 pts. H_2O at 15° C.	...	S.
Bromide of aluminium	Al_2Br_6	V.S.	...	V.S.

SOLUBILITY TABLE—*continued.*

Substance.	Formula.	Water.	Acids.	Alcohol.
Bromide of ammonium .	NH_4Br	V.S.	...	Sp.S.
,, antimony .	$SbBr_3$	Decomposed	...	S.
,, arsenic . .	$AsBr_3$	,,	...	...
,, barium . .	$BaBr_2.2Aq$	V.S.	...	V.S.
,, bismuth .	$BiBr_3$	Decomposed	...	S.
,, boron . .	BBr_3	,,	...	Decomposed
,, cadmium .	$CdBr_2$	V.S.	...	S.
,, calcium . .	$CaBr_2$	V.S.	...	V.S.
,, cobalt . .	$CoBr_2$	V.S.	...	S.
,, copper (ous) .	Cu_2Br_2	Ins.	S. HCl and HBr	...
,, ,, (ic) .	$CuBr_2.5Aq$	V.S.	...	...
,, gold . .	$AuBr_3$	S.	...	...
,, iron (ic) .	Fe_2Br_6	V.S.	...	S.
,, lead . .	$PbBr_2$	Sp.S.	S. HCl, HNO_3 and CH_3COOH	...
,, lithium . .	$LiBr$	V.S.	...	...
,, magnesium .	$MgBr_2.6Aq$	V.S.	...	S.
,, manganese .	$MnBr_2$	V.S.	...	...
,, mercury (ous)	Hg_2Br_2	Ins.	S. hot conc. H_2SO_4 and HNO_3	Ins.
,, ,, (ic) .	$HgBr_2$	S. to V.S.	...	V.S.
,, nickel . .	$NiBr_2.3Aq$	V.S.	...	V.S.
,, potassium .	KBr	V.S.	...	S.
,, silver . .	$AgBr$	Ins.	...	...
,, sodium . .	$NaBr$	V.S.	...	Sp.S.
,, strontium .	$SrBr_2$	V.S.	...	Sp.S.
,, tin (ous) .	$SnBr_2$	S.	...	...
,, ,, (ic) . .	$SnBr_4$	V.S.	...	...
,, zinc . .	$ZnBr_2$	V.S.	...	S.
Carbonates of ammonium	$(NH_4)_2CO$ ...	V.S. Decomposed on boiling	...	...
Carbonate of barium .	$BaCO_3$	Sp.S.	S. CO_2H_2O	...
,, bismuth .	$Bi_2O_3.CO_2$	Ins.	S.	...
,, cadmium .	$CdCO_3$	Ins.	S.	...
,, calcium .	$CaCO_3$	Sp.S.	S. CO_2H_2O	...
,, copper (Basic)	$CuCO_3.Cu(OH)_2$	Ins.	S.	...
,, iron (ous) .	$FeCO_3$	Ins.	S.	...
,, lead . .	$PbCO_3$	Sp.S.	S. HNO_3	...
,, lithium .	Li_2CO_3	S. (hot H_2O)	S.	...
,, magnesium .	$MgCO_3+...H_2O$	Sp.S.	S.	...
,, manganese .	$MnCO_3$	Ins.	S.	...
,, mercury (ous)	Hg_2CO_3	Decomp'd hot H_2O	S. HNO_3	...
,, ,, (ic)	$4HgO.CO_2$	Ins.	S.	...
,, nickel .	$NiCO_3+..H_2O$	Ins.	S.	...
,, potassium .	K_2CO_3	V.S.	S.	Ins.
Bicarbonate of potassium	$KHCO_3$	V.S.	S.	Ins.
Carbonate of sodium .	Na_2CO_3	V.S.	S.	Ins.
,, strontium .	$SrCO_3$	Sp.S.	S. $CO_2.H_2O$	...
,, zinc . .	$ZnCO_3$	Ins.	S.	...
Chlorates . . .	$M'ClO_3$....	S.	...	Mostly all S.; Ins. Ba
Chloride of aluminium .	Al_2Cl_6	V.S.	...	V.S.
,, ammonium .	NH_4Cl	V.S.	...	Sp.S.
,, antimony .	$SbCl_3$	Decomposed	S. HCl	S.
,, arsenic . .	$AsCl_3$	,, by much H_2O	S. HCl	S.

SOLUBILITY TABLE—*continued.*

Substance.	Formula.	Water.	Acids.	Alcohol.
Chloride of barium	$BaCl_2+2Aq$	V.S.	...	Ins.
,, bismuth	$BiCl_3$	Decomposed	S. HCl	S.
,, cadmium	CCl_2+2Aq	V.S.	...	S.
,, calcium	$CaCl_2,6Aq$	V.S.	...	V.S.
,, chromium (ic)	$CrCl_6$ (violet)	V.S.	...	V.S.
,, cobalt	$CoCl_2$	V.S.	...	V.S.
,, copper (ous)	Cu_2Cl_2	Ins.	S. HCl (conc.)	Ins.
,, ,, (ic)	$CuCl_2+Aq$	V.S.	...	V.S.
,, gold	$AuCl_3$	V.S.	S. HCl	S.
,, iodine	ICl	Decomposed	...	S.
,, iron (ous)	$FeCl_2$	V.S.	...	V.S.
,, ,, (ic)	Fe_2Cl_6	V.S.	...	S.
,, lead	$PbCl_2$	Sp.S. (cold) S. (hot)	...	Ins.
,, lithium	LiCl	V.S.	...	V.S.
,, magnesium	$MgCl_2$	V.S.	...	V.S.
,, manganese	$MnCl_2$	V.S.	...	V.S.
,, mercury (ous)	Hg_2Cl_2	Ins.	Decom. by warm HCl	Ins.
,, ,, (ic)	$HgCl_2$	S. to V.S.	...	V.S.
,, nickel	$NiCl_2$	Sp.S.	...	S.
,, platinum	$PtCl_4$	V.S.	...	S.
,, potassium	KCl	V.S.	...	Sp.S. to Ins.
,, silver	AgCl	Ins.	S. HCl (conc.)	...
,, sodium	NaCl	S.	...	Sp.S. to Ins.
,, strontium	$SrCl_2+6Aq$	V.S.	...	Ins.
,, tin (ous)	$SnCl_2+2Aq$	V.S.	S. HCl	S.
,, ,, (ic)	$SnCl_4$	V.S.	...	V.S.
,, zinc	$ZnCl_2$	V.S.	...	V.S.
Chloroplatinates	M'_2PtCl_6	S. or Sp.S.	...	Some S., some Ins.
Chromic acid	H_2CrO_4	V.S.	...	S.
Chromates of NH4, Co, Ca, Cu, Mg, Mn, *Hg'', Ni, K, Na, *Sr, Zn	M'_2CrO_4 ...	S. *Sp.S.	...	...
Chromates of Al, Sb, Ba, Bi, Cr, Be, Fe^{iv}, Pb, Hg', Ag, &c.	,,	Ins.	...	...
Citric acid	$C_6H_8O_7$	V.S.	...	V.S.
Citrates	$M'_3C_6H_5O_7$	Mostly S.	...	...
Cyanate of potassium	KCNO	S.	...	Ins. cold absolute
Cyanogen	CN	S.	...	S.
Cyanides of alkalies, alk. earth and of Hg''	M'CN	V.S.	...	Almost Ins.
Others	...	Ins.	...	...
Ferricyanic acid	$H_6Fe_2(CN)_{12}$	V.S.	...	V.S.
Ferricyanides of NH4, Ba, Ca, *Pb, Mg, K, Na	$M'_6Fe_2(CN)_{12}$..	S. *Sp.S.	...	...
Ferrocyanic acid	$H_4Fe(CN)_6$	V.S.	...	S.
Ferrocyanides of NH4, Ba, Ca, Mg, K, Na, Sr	$M'_4Fe(CN)_6$...	S. to V.S.	...	...
Hydrofluoric acid	HF	S.	...	S.
Fluoride of aluminium	Al_2F_6	Ins.	Ins.	...
,, ammonium	NH_4F	V.S.	...	Sp.S.
,, barium	BaF_2	Sp.S.	S.	...
,, bismuth	BiF_3	Ins.	...	Ins.
,, chromium	Cr_2F_6	S	...	...

SOLUBILITY TABLE—*continued.*

Substance.	Formula.	Water.	Acids.	Alcohol.
Fluoride of calcium	CaF_2	Sp.S.	S. conc. acids	...
,, cobalt	CoF_2+2Aq	Sp.S.	S. HF	Ins.
,, copper (ous)	Cu_2F_2	Ins.	...	...
,, ,, (ic)	CuF_2	Difficultly S.	...	...
,, iron (ous)	$FeF_2+..Aq$	,,	S. HF	...
,, ,, (ic)	Fe_2F_6	Sp.S.	...	Ins.
,, lead	PbF_2	Sp.S.	S. HCl and HNO_3	...
,, lithium	LiF	Sp.S.	...	...
,, magnesium	MgF_2	Ins,	Nearly Insol.	...
,, manganese (ic)	Mn_2F_6	V.S.	...	...
,, mercury (ous)	Hg_2F_2	Decomposed	...	...
,, ,, (ic)	HgF_2	Decomposed	...	...
,, nickel	NiF_2	Sp.S.	S. HF	...
,, platinum (ic)	PtF_4	V.S. (cold)	...	...
,, potassium	KF	V.S.	...	Sp.S.
,, silicon	SiF_4	S. with decomp.	...	S.
,, silver	AgF	V.S.	...	...
,, sodium	NaF	S.	...	Ins.
,, tin (ous)	SnF_2	V.S.	...	...
,, zinc	ZnF_2	Sp.S.	S.	Ins.
Fluosilicates	M'_2SiF_6...	Mostly S. or Sp.S.	...	...
Hydriodic acid	HI	V.S.	...	S.
Indigo	C_8H_5NO	Ins.	H_2SO_4 (fuming)	Ins.
Iodic acid	HIO_3	V.S.	...	Ins. in absolute
Iodates, except those of the alkalies	...	Ins.	...	Ins.
Iodide of aluminium	Al_2I_6	S.	...	S.
,, ammonium	NH_4I	V.S.	...	V.S.
,, antimony	SbI_3	Decomposed	...	...
,, arsenic	AsI_3	V.S. (hot)	...	S. in hot
,, barium	BaI_2	V.S.	...	V.S.
,, bismuth	BiI_3	Decomposed	...	S.
,, cadmium	CdI_2	V.S.	...	V.S.
,, calcium	CaI_2	V.S.	...	S.
,, chromium (ic)	Cr_2I_6	Sp.S. to S.	...	...
,, cobalt	CoI_2	V.S.	...	V.S.
,, copper (ous)	Cu_2I_2	Ins.	...	Ins.
,, gold (ous)	AuI	Ins. (cold), decomp. (hot)	...	Decomposed
,, ,, (ic)	AuI_3	Ins. (cold)	...	...
,, iron (ous)	FeI_2+4Aq	V.S.	...	V.S.
,, lead	PbI_2	Sp.S. (cold), S. (hot)	...	...
,, lithium	LiI	V.S.	...	...
,, magnesium	MgI_2	V.S.	...	S.
,, manganese	MnI_2	V.S.	...	...
,, mercury (ous)	Hg_2I_2	Sp.S.	...	...
,, ,, (ic)	HgI_2	Sp.S.	...	S.
,, nickel	NiI_2+6Aq	V.S.	...	...
,, platinum (ous)	PtI_2	Ins.	Decomposed by HI	...

SOLUBILITY TABLE—*continued.*

Substance.	Formula.	Water.	Acids.	Alcohol.
Iodide of platinum (ic) .	PtI_4	Ins.	...	Sp.S.
,, potassium . .	KI	V.S.	...	S.
,, silver . .	AgI	Ins.	...	...
,, sodium . .	NaI	V.S.	...	S.
,, strontium . .	SrI_2	V.S.	...	...
,, tin (ous) . .	SnI_2	Sp.S.	...	...
,, ,, (ic) . .	SnI_4	Decomposed	...	S.
,, zinc . . .	ZnI_2	V.S.	...	S.
Molybdates . . .	M'_2MoO_4	Alkaline S., others Sp.S. to Ins.	...	...
Nitrates	$M'NO_3$ . . .	S.	...	...
,, Pb, Ni, K, Na, Sr	...	S.	...	Ins.
Nitrites except Ag . .	$M'NO_2$	S.	...	S.
Oxalic acid . . .	$C_2H_2O_4+2Aq$	S.	...	S.
Oxalate of aluminium .	$Al_2C_6O_{12}$	Ins.	S. in dilute	Sp.S.
,, ammonium .	$(NH_4)_2C_2O_4+Aq$	S.	...	Ins.
,, barium . .	BaC_2O_4+Aq	Sp.S.	...	Ins.
,, bismuth .	$Bi_2C_6O_{12}+15Aq$	Ins.	S.	...
,, cadmium .	CdC_2O_4+2Aq	Ins.	S.	Ins.
,, chromium .	$Cr_2C_6O_{12}$	S.	...	...
,, calcium . .	CaC_2O_4	Ins.	Insol. in $C_2H_2O_4$ and $C_2H_4O_2$	...
,, cobalt . .	CoC_2O_4+2Aq	Ins.	...	...
,, copper . .	CuC_2O_4+Aq	Ins.	...	...
,, iron (ous) .	FeC_2O_4+2Aq	Ins.	...	...
,, ,, (ic) . .	$Fe_2C_6O_{12}$	Ins.	S. in $C_2H_2O_4$ and others	...
,, lead . .	PbC_2O_4	Ins.	$C_2H_2O_4$ (hot)	S.
,, lithium . .	$Li_2C_2O_4$	V.S.	...	Ins.
,, magnesium .	MgC_2O_4+2Aq	Sp.S.	...	Sp.S.
,, manganese .	MnC_2O_4	Ins.	S. mineral acids	Ins.
,, mercury (ous) .	$Hg_2C_2O_4+Aq$	Ins.	...	Ins.
,, ,, (ic) .	HgC_2O_4+Aq	Ins.	...	Ins.
,, nickel . .	NiC_2O_4+2Aq	Ins.	...	...
,, potassium .	$K_2C_2O_4+Aq$	S.	...	Ins.
,, sodium . .	$Na_2C_2O_4$	Sp.S.	...	Ins.
,, strontium .	SrC_2O_4	Ins.	...	...
,, tin (ous) . .	SnC_2O_4	Sp.S.	Sp.S. (dilute cold)	...
,, zinc . .	ZnC_2O_4+2Aq	Ins.	S.	...

SOLUBILITY TABLE—*continued.*

Substance.	Formula.	Water.	Acids.	Alcohol.	Other Solvents.
Oxides of aluminium .	Al_2O_3	...	S. in fuming HCl	...	...
,, ,, (hydrated)	$Al_2H_6O_6$	Ins.	...	...	S. KOH, NaOH Sp. S. NH_4OH
,, antimony .	Sb_2O_3	Sp. S.	S. $C_4H_6O_6$ — $C_2H_4O_2$ HCl	...	S. conc. alk. sol.
,, arsenic . .	As_2O_3	S.	S.	...	...
,, barium . .	BaO	Sp. S.	...	S.	...
,, ,, (hydrated)	$BaH_2O_2 + 8Aq$	V.S. (hot)	S. HCl —HNO_3 (dilute)	S.	...
,, bismuth . .	Bi_2O_3	Ins.	S.	...	S. KOH
,, cadmium .	CdO	Ins.	S.	...	S. NH_4OH
,, calcium . .	CaO	Sp. S.	S.	Ins.	...
,, chromium .	Cr_2O_3	Ins.	Ins. HCl	Ins.	...
,, ,, (hydrated)	$Cr_2H_6O_6$	Ins.	S.	...	S. caustic alk.
,, cobalt . .	CoO	Ins.	S.	...	S. (hot) KOH
,, ,, (hydrated)	CoH_2O_2	Ins.	...	...	S. NH_4OH
,, copper (ous) .	Cu_2O	Ins.	S.	...	Sp. SKOH
,, ,, (ic) .	CuO	Ins.	S.	...	S KOH
,, ,, (hydrated)	CuO_2H_2	Ins.	S.	...	S. NH_4OH
,, gold (ous) .	Au_2O	...	S. HNO_3 + HCl	...	...
,, ,, (ic) .	Au_2O_3	Ins.	S. HCl and HCl + HNO_3	...	...
,, iron (ous) .	FeO	Ins.	S.	...	...
,, ,, (ic) .	Fe_2O_3	...	S. HCl	...	...
,, ,, (hydrated)	$Fe_2H_6O_6$	...	S. HCl	...	...
,, lead . .	PbO	...	S. $C_2H_4O_2$ —HNO_3	...	S. caustic alk.
,, lithium . .	Li_2O	S.	...	Sp. S.	...
,, magnesium .	MgO	Sp. S.	S.	...	...
,, manganese .	MnO	Ins.	S.	Ins.	S. NH_4Cl (boiling)
,, ,, .	MnO_2	Ins.	S. HCl. Cl evol'd	Ins.	...
,, mercury (ous)	Hg_2O	Ins.	Ins. HCl and HNO_3 (dilute)	Ins.	S. NH_4Cl
,, ,, (ic) .	HgO	Ins.	S.	...	...
,, nickel . .	NiO	Ins.	S.	...	...
,, ,, . .	Ni_2O_3	...	S.	...	S. NH_4 OH with reduction
,, platinum (ous)	PtO	...	S. H_2SO_3 —H_2SO_4 (conc.)	...	...
,, potassium .	K_2O	V.S.	...	...	...
,, silver . .	Ag_2O	Sp. S.	S. HNO_3	...	S. NH_4OH
,, sodium . .	Na_2O	V.S.	...	...	...
,, strontium .	SrO	S.	...	Sp. S.	...
,, tin (ous) . .	SnO	Ins.	S.	...	...
,, ,, (ic) . .	SnO_2	Ins.	S. (conc.) H_2SO_4	...	...

SOLUBILITY TABLE—*continued.*

Substance.	Formula.	Water.	Acids.	Alcohol.	Other Solvents.
Oxides of zinc	ZnO	Ins.	S.	...	...
Oxychlorides	...	Mostly Ins.	...	...	...
Oxybromides	...	,,	...	...	...
Oxyiodides	...	,,	...	...	...
Perchlorates	$M'ClO_4$	V.S. to S.	...	...	...
Periodates	...	Mostly Ins., alkalis S.	S. HNO_3	...	...
Peroxides	Variable	Na_2O_2 and K_2O_4 S. with decomp.	S. with decomp.	...	...
Permanganates	$M'MnO_4$	All S. except $AgMnO_4$, Sp.S.	...	...	...
Phosphoric acid	H_3PO_4	V.S.	...	S.	...
Phosphate of aluminium	$Al_2P_2O_8$	Ins.	S.	...	...
,, ammonium	$H(NH_4)_2PO_4$	V.S.	...	Ins.	...
,, ,,	$(NH_4)_3PO_4$	Sp.S.	...	...	...
,, ,,	$H_2(NH_4)PO_4$	V.S.	...	...	...
,, barium	$BaHPO_4$	Sp.S.	S. Dilute HCl, H_3PO_4 HNO_3	...	...
,, cadmium	$Cd_3P_2O_8$	Ins.	...	...	S. cold NH_4Cl
,, calcium	$Ca_3P_2O_8$	Ins.	S. HNO_3 —HCl	Ins.	...
,, chromium	$Cr_2P_2O_8$	Ins.	S.	...	...
,, cobalt	$Co_3P_2O_8+xAq$	Ins.	S.	...	S. NH_4OH
,, copper	$CuHPO_4$	Ins.	S.	...	...
,, iron (ic)	$Fe_2P_2O_8$	Ins.	S. V.Sp.S. $C_2H_4O_2$	...	...
,, lead	$Pb_3P_2O_8$	Ins.	S. HNO_3 Ins. $C_2H_4O_2$	...	Ins. NH_4OH
,, lithium	LiH_2PO_4	V.S.	...	...	...
,, ,,	Li_3PO_4	Sp.S.	S. Very dilute acids and CO_2H_2O	...	...
,, magnesium	$H_4MgP_2O_8$	V.S.	...	...	...
,, ,,	$MgHPO_4+7Aq$	S.	S. dilute	Ins.	...
,, ,,	$Mg_3P_2O_8$ +5 or 7Aq	Ins.	S. dilute	...	...
,, and amm.	$(NH_4)_2Mg_2P_2O_8+12Ag$	V.Sp.S.	S.	...	...
,, manganese	$Mn_3P_2O_8+7Aq$	Sp.S.	S.	Ins.	..
,, mercury (ous)	$Hg_6P_2O_8$	Ins.	Decomposed by HCl	...	...
,, (ic)	$Hg_3P_2O_8$	Ins.	S.	...	...
,, nickel	$Ni_3P_2O_8+7Aq$	Ins.	S.	...	...
,, potassium	KH_2PO_4	V.S.	...	Ins.	...
,, ,,	K_2HPO_4	V.S.	...	V.S.	...
,, ,,	K_3PO_4	V.S.	...	Ins.	...

SOLUBILITY TABLE—*continued.*

Substances.	Formula.	Water.	Acids.	Alcohol.	Other Solvents.
Phosphate of silver	Ag_3PO_4	Decomp'd	S. HNO_3	Ins.	...
,, ,,	Ag_3PO_4	Ins.	S. HNO_3; S. NH_4OH; S. H_3PO_4; S. $C_2H_4O_2$	...	S. NH_4OH, KCN, NH_4Cl
,, sodium	$NaH_2PO_4 + Aq$	V.S.	...	Ins.	...
,, ,,	$Na_2HPO_4 + 12Aq$	S. to V.S.	...	Ins.	...
,, ,,	$Na_3PO_4 + 12Aq$	V.S.	...	...	...
,, strontium	$SrHPO_4$	Ins.	S.	...	...
,, tin (ous)	$Sn_2P_2O_7$	Ins.	S.	...	S. NH_4OH, KCN, KOH
,, ,, (ic)	$5SnO.P_2O_5 + 10Aq$	...	Ins. HNO_3	...	...
,, zinc	$Zn_2P_2O_7 + 4Aq$	Ins.	S.	...	S. NH_4OH, KCN, KOH
Selenates	M_2SeO_4	S. except Ba, Ce, Ca and Pb	Sp.S. to Ins. HNO_3	...	...
Selenides	M_2Se	Alkaline S.	S. HNO_3	...	...
Silicates	...	Na and K silicates, mostly S. Others Ins.	Some decomposition, all decomp. by HF	...	...
Stannates	M_2SnO_3	Alkaline S.	S.	...	...
Succinates	...	Mostly S.	...	...	S. HCl, H_2O
Sulphate of aluminium	$Al_2(SO_4)_3 + 18Aq$	V.S.	...	Ins.	...
,, ammonium	$(NH_4)_2SO_4$	V.S.	...	Ins.	...
,, barium	$BaSO_4$	Ins.	Sp.S. in dilute	Ins.	...
,, cadmium	$CdSO_4 + 4Aq$	S.	...	Ins.	...
,, calcium	$CaSO_4$	Sp.S.	Sp.S. to S.	...	...
,, chromium	$Cr_2(SO_4)_3 + 18Aq$	V.S.	S.	S.	...
,, cobalt	$CoSO_4$	Sp.S. (cold)	...	Sp.S.	...
,, copper (ous)	Cu_2SO_4	Ins.	Ins. conc. H_2SO_4	...	...
,, ,, (ic)	$CuSO_4 + 5Aq$	V.S.	...	Sp.S.	...
,, iron (ous)	$FeSO_4 + 7Aq$	V.S.	...	Ins.	...
,, (ic)	$Fe_2(SO_4)_3 + xAq$	V.S.	...	S.	...
,, lead	$PbSO_4$	Sp.S.	...	Ins.	...
,, lithium	$Li_2SO_4 + Aq$	V.S.	...	Sp.S.	...
,, magnesium	$MgSO_4 + 7Aq$	V.S.	...	Sp.S.	...
,, manganese	$MnSO_4$	V.S.	...	Ins.	...
,, mercury (ous)	Hg_2SO_4	Sp.S.	S. dil. HNO_3	...	...
,, ,, (ic)	$HgSO_4$	Decomposed	S. hot conc. HCl	Ins.	...
,, nickel	$NiSO_4 + 7Aq$	V.S.	...	Sp.S.	...
,, potassium	K_2SO_4	S. to V.S.	...	Ins.	...
,, silver	Ag_2SO_4	S.	S.	Ins.	...
,, sodium	Na_2SO_4	V.S.	...	Sp.S.	...
,, strontium	$SrSO_4$	Sp.S.	...	Ins.	...
,, zinc	$ZnSO_4$	V.S.	...	Ins.	...
Sulphide of aluminium	Al_2S_3	Decomposed	...	...	...

SOLUBILITY TABLE—*continued.*

Substance.	Formula.	Water.	Acids.	Alcohol.	Other Solvents.
Sulphide of ammonium .	$(NH_4)_2S$	S.	...	...	...
,, antimony (ous)	Sb_2S_3	Ins.	S. HCl (conc.)	Ins.	S. caustic alkalis and alk. sulphides
,, ,, (ic)	Sb_2S_5	Ins.	,,	Ins.	S. NH_4HS
,, arsenic . .	As_2S_3	Ins.	Ins. HCl	...	S. caustic alkalis and alk. sulphides
,, barium .	BaS	S. with decomp.	S.	Ins.	...
,, bismuth .	Bi_2S_3	Ins.	Ins. dilute S. HCl (hot)	...	...
,, cadmium .	CdS	Ins.	S. (conc.)	...	...
,, calcium .	CaS	Sp.S.	S.	...	...
,, chromium .	Cr_2S_3	Ins.	S. HNO_3 and HCl + HNO_3	...	Ins. KOH + K_2S
,, cobalt . .	CoS	Ins.	Sp.S. (dil.) S. HCl + HNO_3	...	...
,, copper (ous) .	Cu_2S	Ins.	S. HNO_3 (hot)	Ins.	...
,, ,, (ic) .	CuS	Ins.	S. (conc.)	...	...
,, gold . .	Au_2S_3	Ins.	S. HCl + HNO_3	...	S. NH_4HS
,, iron . .	FeS	Ins.	S.	Ins.	...
,, lead . .	PbS	Ins.	S. hot conc. HNO_3 (with decomp.)	...	...
,, lithium .	Li_2S	S.	...	S.	...
,, magnesium .	MgS	Sp.S. with decomp.	S. with decomp.	...	...
,, manganese .	MnS	Ins.	S.	...	...
,, mercury (ous)	Hg_2S	Ins.	Ins. dilute HNO_3	...	S. KOH
,, ,, (ic)	HgS	Ins.	S. HCl + HNO_3	...	S. Na_2S and K_2S
,, nickel . .	NiS	Ins.	S. HCl + HNO_3	...	...
,, potassium .	K_2S	S.	...	S.	...
,, silver . .	Ag_2S	Ins.	S. conc. HCl and HNO_3	...	...
,, sodium .	Na_2S	S.	...	Sp.S.	...
,, strontium .	SrS	S. with decomp.	...	S	...
,, tin (ous) .	SnS	Ins.	S. HCl (conc.)	...	S. $(NH_4)_2S_2$ or K_2S
,, ,, (ic) .	SnS_2	Ins.	S. HCl (conc.)	...	S. caustic alkalis and alk. sulphides
,, zinc . .	ZnS	Ins.	S.	...	Ins. caustic alkalis
Sulphite of ammonium .	$(NH_4)_2SO_3$	V.S.	...	Sp.S.	...
,, barium . .	$BaSO_3$	Sp.S.	S. H_2SO_3	...	...
,, cadmium .	$CdSO_3$	Sp.S.	...	Ins.	...
,, calcium .	$CaSO_3$	Sp.S.	S. H_2SO_3	...	...
,, cobalt . .	$CoSO_3$	Sp.S.	...	Ins.	...

SOLUBILITY TABLE—*continued.*

Substance.	Formula.	Water.	Acids.	Alcohol.	Other Solvents.
Sulphite of lead	$PbSO_3$	Ins.	Sp.S. H_2SO_3	...	...
,, lithium	Li_2SO_3+6Aq	S.	...	Ins.	...
,, magnesium	$MgSO_3+6Aq$	S.	S. H_2SO_3	Ins.	...
,, manganese	$MnSO_3+2Aq$	Ins.	S. H_2SO_3	Ins.	...
,, nickel	$NiSO_3+6Aq$	Ins.	S. H_2SO_3	...	...
,, potassium	K_2SO_3+2Aq	V.S.	...	Sp.S.	...
,, silver	Ag_2SO_3	Sp.S.	Almost Ins. in H_2SO_3	...	...
,, sodium	Na_2SO_3+7Aq	V.S.	...	Ins.	...
,, strontium	$SrSO_3$	Sp.S.	S. H_2SO_3	...	...
,, zinc	$ZnSO_3+2Aq$	Sp.S.	...	Ins.	...
Sulphocyanides	...	All S. except Ag, Hg', Cu', Bi, Cd, Pb	...	...	...
Sulphydrates	...	S. (NH_4), Ba, Ca, K, Na, Sr	...	...	...
Tartaric acid	$C_4H_6O_6$	V.S.	...	V.S.	...
Tartrates	...	S. normal alk. tartrates, the acid less so	All S. HCl and HNO_3	...	All S. in NH_4OH, except Hg
Tellurates	M'_2TeO_4	S. to Sp.S.	S. HNO_3	...	...
Tellurides	M'_2Te	Alkaline S.	S. HNO_3	...	...
Thiosulphates	$M'_2S_2O_3$	Alkaline and Ca, Sr, Ba S. to V.S, others S. to Sp.S.	...	...	...
Titanic acid	...	Ignited (TiO_2) Ins.	Ins. except HF	...	...
,, ,,	...	Hydrated (TiO_2) Ins.	S.	...	...
Tungstates	...	Alk. tungstates S, also Mg; others Ins.	...	...	...
METALS.	Symbol.				
Aluminium	Al	...	S. HCl	...	...
Antimony	Sb	...	S. HCl + HNO_3	...	...
Arsenic	As	...	Ins. HNO_3 oxidises it	...	...
Barium	Ba	Decomposes	...	...	...
Bismuth	Bi	...	S.	...	...
Cadmium	Cd	...	S.	...	...
Calcium	Ca	Decomposes	...	...	...
Chromium	Cr	...	S. HCl – H_2SO_4	...	...

SOLUBILITY TABLE—*continued.*

Substance.	Symbol.	Water.	Acids.	Alcohol.	Other Solvents.
Cobalt	Co	...	S.	...	...
Copper	Cu	...	S.	...	...
Gold	Au	...	S. HCl + HNO_3	...	...
Iron	Fe	...	S	...	...
Lead	Pb	...	S. HNO_3	...	...
Lithium	Li	Decomposes	...	...	...
Magnesium	Mg	Decomposes (hot)	S.	...	...
Manganese	Mn	Decomposes	S.	...	...
Mercury	Hg	...	S.	...	...
Molybdenum	Mo	...	S. HNO_3	...	...
Nickel	Ni	...	S. HCl	...	...
Palladium	Pd	...	S. HNO_3	...	...
Platinum	Pt	...	S. HCl + HNO_3	...	...
Potassium	K	Decomposes	...	...	...
Silicon	Si	...	S. HF	...	...
Sodium	Na	Decomposes	...	...	...
Silver	Ag	...	S. HNO_3	...	...
Strontium	Sr	Decomposes	...	...	...
Tellurium	Te	...	S. H_2SO_4	...	...
Thallium	Tl	...	S. HNO_3	...	...
Tin	Sn	...	S. HCl	...	..
Titanium	Ti	...	S. HCl	...	...
Tungsten	W	...	Ins.	...	Dry Cl dissolves
Uranium	U	...	S.	...	...
Vanadium	V	...	S. H_2SO_4 (conc.)	...	...
Zinc	Zn	...	S.	...	...
Zirconium	Zr	...	S. HF and HCl + HNO_2	...	...

APPARATUS FOR QUANTITATIVE ANALYSIS AND ASSAYING.

The student will require the following apparatus, which he may either purchase or obtain on deposit, making good any breakages according to the practice of the laboratory. Gallenkamp's numbers are again given as a guide, though several other English firms supply goods of equal quality This apparatus is additional to what he already has.

Gallenkamp's Catalogue No.	
1218	2 porcelain crucibles (14 c.c.).
776	2 „ Gooch crucibles (one 10 c.c., one 25 c.c.).
3168	2 desiccators (12 cm.).
20K or 20	2 evaporating dishes, 110 mm.
„	2 „ „ 180 „

Gallenkamp's Catalogue No.	
419	100 filter papers, 10 cm.
„	50 „ „ 7 „
375A	2 Erlenmeyer flasks (250 c.c.).
783	2 pump flasks (500 c.c.).
1204	1 pair forceps.
672	4 funnels, 50 mm.
„	2 „ 25 „
778	2 Gooch funnels and rubber caps.
1413	12 sheets glazed paper (white and black).
1314	1 steel spatula (7 cm.)
1316	1 horn spatula.
3553	1 wash bottle, 250 c.c.
3078	1 weighing bottle.
1663	1 pair watch glasses and clip.
1177, 1178	1 camel's-hair brush, round, and one flat.
2459A	2 burettes, 50 c.c., graduated in tenths of a c.c.
2483	2 floats.
2635	2 cylinders, 100 c.c. and 1000 c.c.
2585	Pipettes, one 10 c.c., one 25 c.c., one 50 c.c., and one graduated.
2900	1 thermometer, 0°–300° C.
1729	6 litre bottles for storing standard solutions.
1411	2 test tiles (eight holes each), porcelain.
1139	1 bead hammer.
1363	1 Cupel tray (sixteen divisions).
1314	1 steel spatula (20 cm.).
1413 ?	12 sheets of glazed paper (stout for assaying).
1229	2 annealing cups.
1408	2 parting bulbs.

Generally the following Apparatus is supplied by the Laboratory :—

Balance.
Water oven, air oven.
Hydrometers.
Diamond mortar, sieves, agate and steel mortars.
Hot plates, combustion furnace and fittings.
All the more complicated glassware and other apparatus.
Furnaces, grinding appliances, furnace tools, gold rolls, etc., required in assaying.
Any special apparatus required in technical analysis.

The student may procure or obtain on deposit—

1 box gram weights.
1 box assay weights.
Platinum crucible (30 c.c.).

Also it will be more convenient if arrangements be made to obtain all crucibles, scorifiers, and other assaying stores from the laboratory stores as required, as such materials take up too much of his locker space. Such stores to be given out once a week.

The above lists include most of the ordinary requirements. Any additional apparatus may be procured during the course.

QUANTITATIVE ANALYSIS.

CHAPTER II.

INTRODUCTORY.

In the course of work completed, the problem so far met with has been the determination of the various elements (or compounds) present in a substance. In an ore, for instance, there may be present silica, iron, copper, arsenic, and sulphur, and it is the province of **qualitative analysis** to determine the presence or absence of these and other elements. It is obvious, however, that there still remains an unknown factor, namely, the quantity of each element present in any given substance. Having found that the ore contains the substances mentioned, the student is now asked how much silica, iron, copper, arsenic, and sulphur by weight are present in one gram or other convenient weight of the ore.

It may be said, then, that the province of **quantitative analysis** lies in the determination of the quantities—either by weight or by volume—of the various elements present in a substance. This substance may be a solid, liquid, or a gas.

Such an analysis may be either *proximate* or *ultimate*. For example, if one gram of salt be mixed with one gram of iron pyrites and the mixture be analysed, we may—

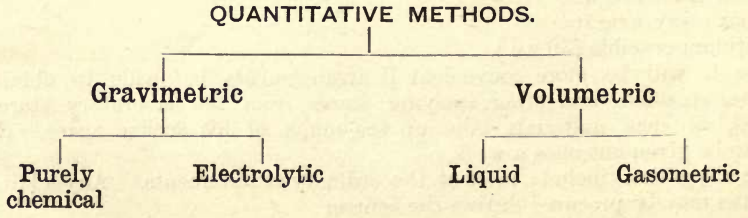
(1) Extract the salt with water and leave the iron pyrites as a residue. By filtering and evaporating the solution to dryness, the salt may be estimated; and by drying and weighing, the iron pyrites may be estimated.

(2) The formula of salt is **NaCl**, and of iron pyrites FeS_2. By methods given further on, we may estimate the **Na**, **Cl**, **Fe** and **S** present by four separate determinations.

In the first case, where *compounds* are determined, the analysis is termed *proximate*.

In the second case, where *elements* are determined, the analysis is termed *ultimate*.

For convenience, quantitative methods may be classified thus:—



GRAVIMETRIC METHODS.

Purely Chemical.

In this section certain gravimetric methods—those of fire-assaying—are omitted. These, on account both of their nature and importance to the metallurgical chemist, are dealt with in a special section in Part III.

Conditions.—As a general rule, in the methods to be given the following conditions hold :—

a. The element to be estimated is generally converted into some compound.
b. This compound is insoluble in the liquid medium present.
c. This compound has a definite, known composition.
d. This compound can be brought into a state suitable for accurate weighing.

Processes.—Though variations in treatment, involving evaporation, digestion, distillation, and other processes, are met with, it may be said that generally the following processes are necessary when estimating an element or elements by "purely chemical" gravimetric methods.

1. **Sampling** and preparing the substance for solution.
2. **Weighing** the quantity taken for analysis.
3. **Solution** of the substance.
4. **Precipitation** of the element sought.
5. **Filtration** of the precipitate thus obtained.
6. **Washing** the precipitate.
7. **Drying,** or drying and **Ignition.**
8. **Weighing** the precipitate.
9. **Calculating** the result.

These operations will be briefly described in turn; and before proceeding to the first estimation given, the student must carefully read through these descriptions, obtain the necessary apparatus and reagents, and check the accuracy of the balance and weights to be used. He must also in every analysis consider the purity or otherwise of the reagents used. This point has already been referred to under "qualitative analysis," and will again be briefly noticed under "miscellaneous instructions."

1. **Sampling.—The Preparation of the Substance for Solution.** — Too much emphasis cannot be laid on the fact that without careful sampling the value of an estimation is practically **nil.** In the majority of cases the chemist is required to determine the percentage of an element or compound present in a considerable mass of the substance given, and (except in the case of chemical salts) it is the safe course to assume that the element to be estimated is distributed *unevenly* throughout the mass. Therefore, to accurately estimate the quantity of the element present in the whole mass, an average sample must be obtained. The sample taken for analysis must have been so taken that it represents the true average contents of the mass.

Discrepancies in the results of different chemists are more frequently due to errors in sampling than to errors of method and manipulation in the analysis itself. When, for example, the student is given a 10 to 15 gram sample of galena, and is instructed to weigh out about ·5 gram for analysis; then, if he wish the results of several consecutive analyses to agree, he must be absolutely certain that, to the best of his ability, he has so selected this ·5 gram lot, that it represents the true average contents of the larger sample.

It is useless for the student to worry his brain searching for defects in

his analytic manipulation, when results do not agree, unless he is perfectly sure that the sampling error cannot account for the discrepancies.

The sole conditions of success are that the best methods and manipulation are preceded by accurate sampling.

The substance to be sampled may be either a *Solid*, *Liquid*, or *Gas*.

A. **Solids.**—The solid presented for analysis may vary from a few ounces to several tons. In this chapter large parcels will not be considered; not that their sampling is unimportant or easy. The reverse is the case. This matter will be considered in the section devoted to Assaying. Here it is assumed that the student is presented with a few ounces of the material either in coarse lumps or as a fine powder.

Sampling small Parcels. — When in the form of coarse lumps reduce the whole sample by pulverising in a cast-iron mortar such as is used in the reduction of ores for assaying. If, however, the substance has chemical action on iron, or is so hard that particles of iron from the mortar become mixed with the sample, special methods of reduction must be resorted to. To avoid chemical reactions occurring, mortars of porcelain or agate must be used, the latter when the substance is hard. To avoid contamination by particles of iron a large "diamond mortar," such as is shown in fig. 37, is used.

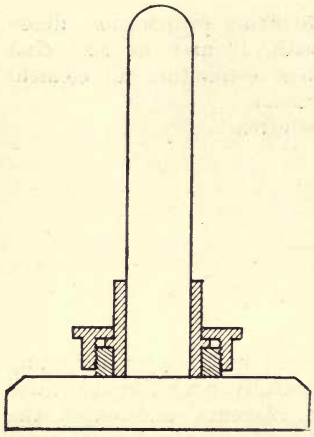


Fig. 37.

This mortar is made of steel "case-hardened," and will be found satisfactory in most cases. Its use is self-evident. The piston being removed, a few small pieces of the solid are inserted, the piston replaced and a few blows smartly struck with a hammer. The powdered solid is then removed and placed on a clean sheet of glazed paper. If the lumps of the solid are too large for the mortar, wrap them one at a time in clean paper; place on a clean anvil and crush with a few blows of a heavy hammer. When the sample has been thus reduced pass the fine material through a 30 sieve. Any particles not passing through the sieve are re-crushed until of the requisite fineness.

No hard and fast rules can be laid down regarding the reduction of various materials. In every case the student must consider first the chemical nature of the solid—*i.e.*, as regards its chemical effect on the reducing appliances; then he must consider its hardness and the probability of mechanical contamination. Generally for chemical salts the Wedgwood mortar may be used; for soft minerals (not harder than 6 Moh's scale) the iron mortar or "bucking plate" (see Assaying); and for harder minerals, etc., the diamond-mortar, though even then there is danger of slight mechanical contamination. The student now has 20 or 30 grams of the solid in a state of fine division. With the "Spatula" (a spatula with a 10 cm. steel blade will be suitable unless chemically acted on by the powder, in which case use vulcanite or platinum), carefully mix the powder by repeatedly turning it over, flattening it out and heaping it up. When thoroughly mixed (a few minutes should suffice), flatten out the heap into the form of a shallow truncated cone. See figs. 38 and 39.

With the spatula divide the heap into quarters as shown. Remove two diagonally opposite quarters. Again mix the remainder and re-quarter as before, till finally by repetition of this process about 5 to 10 grams remain.

If the student is instructed to take from ·5 to 2 grams of the material for each analysis he will have sufficient material for five to ten estimations. If a larger quantity is required for each estimation the sample must be proportionately larger. To obtain some idea of the weight of the sample the student may roughly weigh it on a set of "pulp-scales" (see Assaying).

This sample has now to be ground to such a state of fineness that it is easily soluble in the water, acids, fusion-mixture or other solvent medium to be used. This grinding is almost invariably performed in the agate mortar. As a rule, chemical salts require little additional grinding. Mineral powders, however, generally require prolonged treatment in the agate mortar, which for this propose should be at least 9 cm. in diameter. With smaller mortars progress is painfully slow. The grinding is performed most satisfactorily by placing in the mortar about half a gram of the solid, and then the powder is ground by a circular grinding motion of the pestle, assisted by fair pressure of the hand. This grinding must be continued till on rubbing a small pinch of the powder between the tips of the fingers no grit is felt. Then proceed with another portion, and so on till sufficient is ground for five or six analyses. The finely ground sample is now spread out on a small sheet (20 cm. × 20 cm.) of glazed paper. It is then carefully mixed and flattened out. The portion for analysis is then taken either by systematically dipping with the point of the spatula or by running through the flat-heap small trenches with the edge of the spatula.

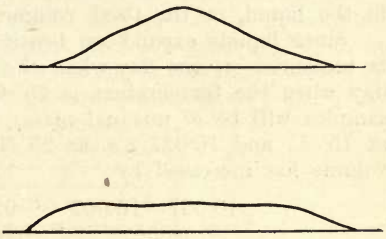


FIG. 38.

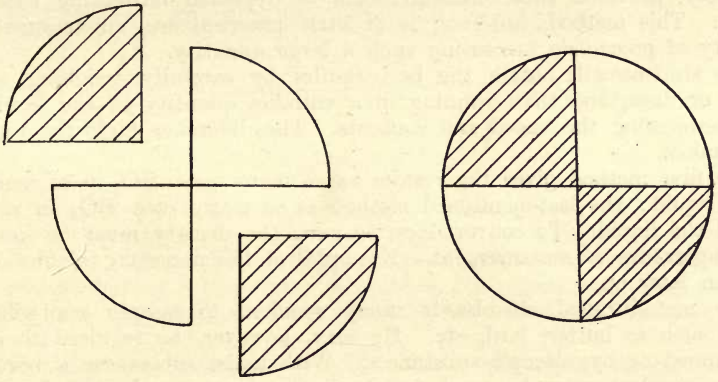


FIG. 39.

The student will find that the thorough reduction of minerals is the most tedious part of the whole analytical process. Though in some cases the process is exceedingly laborious, he must resist every inclination to shirk the thorough reduction of the portion for analysis. In the majority of cases the time and labour required are not excessive, and in the few cases where they appear so it must be remembered that accurate results cannot be obtained otherwise. Of late years power-driven agate mortars have been successfully introduced in technical and other laboratories.

B. **Liquids.**—In most cases the samples presented for analysis are solids. Sometimes, however, the student is asked to determine the quantity of some element or compound present in a liquid. For instance, he may be asked to determine the SO_3 present in a Winchester quart bottle partly filled with H_2SO_4. An average sample can be quickly obtained by shaking the bottle and pouring out the desired quantity. This portion for analysis may be either measured or weighed. It may be measured either from an accurate "pipette" or "burette" (see Volumetric Analysis); but either the temperature of the solution must be carefully noted by immersing a thermometer in the liquid, or the total volume of the solution must be ascertained.

Since liquids expand on heating, it will be seen that if 10 c.c. of water be measured on one day when the temperature is 15° C., and on the following day when the temperature is 25° C., another 10 c.c. lot be measured, the two samples will be of unequal mass. 10 c.c. water at 0° C. become 10·007 c.c. at 15° C. and 10·027 c.c. at 25° C.; that is, between 15° C. and 25° C. the volume has increased by

$$\frac{10{\cdot}027-10{\cdot}007}{10{\cdot}027}=\frac{{\cdot}02}{10{\cdot}027}=\frac{2}{1002{\cdot}7} \text{ or about } \tfrac{1}{500}.$$

The density, which varies inversely as the volume has decreased, therefore, assuming that the acid expands similarly, the sample of 10 c.c. measured at 25° C. contains $\frac{1}{500}$ less SO_3 than the portion measured at 15° C.; that is an error of 0·2 per cent., assuming the solution expands similarly to water.

This matter will be dealt with more fully under "Volumetric Analysis."

If, however, the contents of the bottle be measured in an accurate "Test Measure" (see "Volumetric Analysis"), and are found to be, say, 1600 c.c., and 10 c.c. be taken at the same temperature, the estimation can be made accurately, provided these measurements be repeated on taking each fresh portion. This method, however, is of little practical use, on account of the difficulty of *accurately* measuring such a large quantity.

The student will obtain the best results by carefully weighing a small beaker or flask, and then running in a suitable quantity of the liquid, and then re-weighing the vessel and contents. The difference gives the weight of liquid taken.

The first method gives the results as so many *gms.* SO_3 in so many *c.cs.* of the liquid; the last-mentioned method as so many *gms.* SO_3 in so many *gms.* of the liquid. To convert c.cs. to gms. the density must be known at the temperature of measurement. Examples of the necessary calculations will be given later on.

The metallurgical chemist is rarely required to sample semi-solid substances such as butter, lard, etc. He may, however, be required to analyse either moist or hygroscopic substances. With moist substances a boring rod (cheese sampler) may be used to obtain an average sample. In this the moisture is determined (see Assaying), and the dry sample is assayed as usual. Certain hygroscopic substances present some difficulty, as they rapidly absorb moisture from the air. With these quickly pick from the containing jar an average sample, weighing it quickly and accurately on the pulp scales. It may then be dissolved in water, and treated as a liquid.

C. **Gases.**—The methods of collecting these are described or referred to in the section on Technical Analysis, and the student is there referred to certain authorities on this subject. In this section the subject is not touched on.

2. **Weighing the Substance.**—In gravimetric analysis the method of

measurement adopted is that of weighing—one of the most accurate means we possess—and by it the student may with ease and rapidity weigh objects of 100 gms. accurately to ·001 gm., that is, with an error of less than $\frac{1}{100,000}$ Or again he may weigh 1 gm. accurately to ·0001 gm., an error of less than $\frac{1}{10,000}$.

Before proceeding to describe the operation of weighing, the various methods of weighing, and the selection of a suitable weight of the substance, a description of the balance, weights, and accessories is necessary.

The Balance.—In this place it will be sufficient to describe the usual chemical balance, designed to carry in each pan a load up to 100 gms. This balance can be obtained at a reasonable figure, and sensitive to $\frac{1}{10}$ of a milligram (0·0001 gm.). In the section on Assaying the student will find two other forms—Pulp Scales and the Assay Balance—mentioned. The pulp

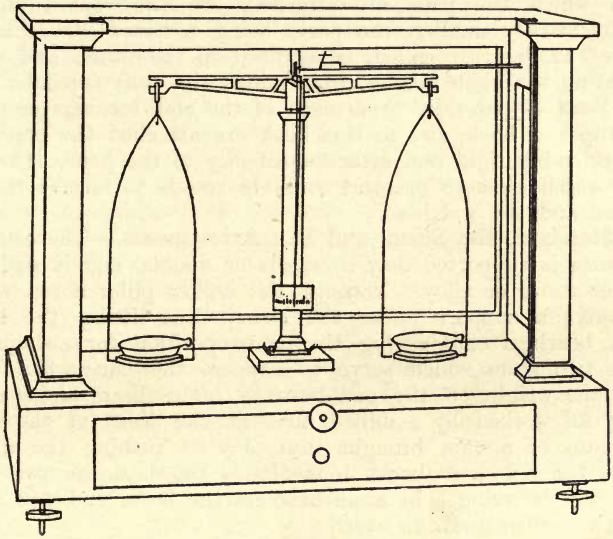


Fig. 40.

scales are cheap, and sensitive to about $\frac{1}{100}$ gm., and serve well for weighing quantities of 20 gms. and over. The assay balance is more sensitive than the chemical balance, but its range is shorter (from ·5 gm. to ·00005 gm.). The student who understands the chemical balance, its adjustments and methods of checking and weighing, will have little difficulty in using the finer assay balance.

The Parts of the Balance.—(*a*) **The Beam.**—This is generally made of brass or aluminium, and varies in shape and length. Fig. 40 shows one design (Ainsworth, U.S.A.). A short beam is preferable to a long one, the time of vibration being shortened, and the increased lightness permitting higher sensibility. One end of the beam is always graduated, though it is advisable to have both ends graduated, each into 10 divisions marked 1, 2, 3, . . . 8, 9, 10. Each of these divisions is again divided into five parts. Other graduations are met with, and the student, when he meets with them, must find their value in terms of the pan weights (see the following). Attached to the beam is either a small movable vane on the top edge, at the centre, or one or two movable milled heads, working along horizontal screws, on the extremities of the beam. These devices are for the purpose of altering the centre

of gravity of the beam in a horizontal direction, thus causing it to swing at will more one way than the other. Attached to the centre of the beam by a small bracket is a long pointer, at right angles to the length of the beam, and pointing downwards. The fine extremity of this pointer passes in front of a small ivory scale, graduated on each side of the centre into ten equal parts, as in fig. 41.

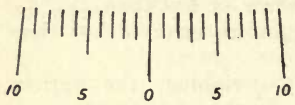


FIG. 41.

The use of this scale will be seen under "Methods of Weighing."

On the beam are three bearings—one at the centre and one at each end. The centre bearing, on which the beam swings, consists of a triangular prism of steel or agate, attached to the beam by one of its faces, with its free edge bearing on a flat agate plate on the top of the standard. The end bearings, to which the pans are attached, are somewhat similar in construction, but usually smaller, the parts being reversed—*i.e.* the prisms or "knife edges," as they are called, being fixed in the beam, and their upper edges supporting the agate planes, from which the pans depend.

(*b*) **The Pans.**—Suspended from each of the end bearings as described is a small stirrup and hook, and to this hook are attached the pan suspenders, which are preferably rigid and attached directly to the pans. On these pans are placed "watch glasses" or other suitable vessels to receive the substance to be weighed and the weights.

(*c*) **The Standard, the Beam, and Pan Arrestments.**—The centre post on which the beam is supported may be single or double, and is made of hollow brass or other metal or alloy. Through the hollow pillar a rod works which raises or lowers a support under the beam, thus lifting the knife edges off the agate bearings or lowering them into position for swinging. Under the pans are two stops which serve to support the pans when not in use and to take the weight off the end bearings. The beam and pan supports are generally all worked by a milled head at the front of the base of the case. By means of a cam brought into play on turning the milled head, the stops are lowered and almost immediately the beam support drops and the beam is free to swing. In some balances the beam and pan motions are operated by two milled heads, in which case the pan supports are first freed and then the beam support.

(*d*) **The Case.**—This is generally of mahogany with glass sides, front, back and top, and plate-glass base-plate. In front is a sliding door, and below are two small drawers for the necessary accessories. At the sides are the arms for operating the rider on the beam. When not in use the case is closed and carefully enclosed in a dust-proof cover of green baize with Mackintosh lining. The balance table must be solid and free from vibration, and the balance beam must be well lighted.

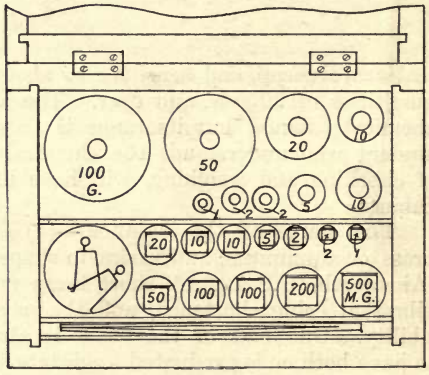


FIG. 42.

The Weights.—It is advisable that the metallurgical student purchase a set of weights for his own use. A set costing about £3 will, with care, last a lifetime, and if made by such firms as "Oertling" or "Becker & Sons," they can be relied on for accuracy (see fig. 42). A set ranging from

50 grams to ·001 grams with riders will answer all purposes. The brass weights in the box give the grams; the larger foil weights, marked either ·5, ·2, ·2, ·1, or 500, 200, 200, 100, give the decigrams, and the smaller foil weights, marked ·05, ·02, ·02, ·01, or 50, 20, 20, 10, give the centigrams. Many sets of weights include still smaller foil weights, but these are superfluous, as the milligrams are obtained by using the rider on the beam, the whole numbers on the beam representing milligrams when the rider weighs one centigram and the beam is divided into ten equal parts. Fractions of a milligram are read from the subdivisions between the whole numbers. Some makers subdivide their weights thus: 10, 5, 2, 1, 1, 1; some thus: 10, 5, 2, 2, 1; and some thus: 10, 5, 3, 2, 1, and so on. The weights are handled by the forceps provided.

Methods of checking the Accuracy of the Balance and Weights.—When obtained at a fair price from a good maker, the balance and weights are generally sufficiently accurate for the student's purpose; but, in order that he may gain an insight into the principle of the balance and the magnitude of error (if any) that may arise from defects in the balance and weights the *Ostwald's* incomplete scheme is laid down. (For fuller information consult following *Physico-chemical Measurements.*)

A. **Checking the Balance.**—Having seated himself on a stool of convenient height, the cloth cover is removed and the student is ready to test the accuracy of the balance, his note-book and set of weights being at his hand. See that the balance is level, adjusting, if necessary, the base thumb-screws. Gently turn the milled head and release the beam, so that it swings four to five divisions right and left on the pointer scale (that is, about half-way across). When reading this scale keep the eye opposite the zero point in all cases. If in proper order, the pan stops should drop just slightly ahead of the beam rest and the beam should swing gently. The whole movement must be gradual and without any sudden jerk. (If unsatisfactory, refer the matter to the demonstrator; do not at present attempt to rectify it without aid.)

If the beam swings more to one side than the other, arrest it. Then, with a broad camel's-hair brush, carefully dust the pans and top of the beam. Again try the swing, and if no better, then adjust it by *slightly* moving the centre vane towards the lighter side, or by moving the end screw towards the lighter side. Try the swing, and repeat till the centre of the swing is one division from the centre of the scale. If, for instance, the pointer swings four right and three left, it will come to rest at +1, or the centre of the swing is one division to the right.

The student will now proceed to test—

(*a*) **The Sensitiveness of the Balance under Different Loads.**—Release the balance to swing between +6 (on the right) and −6 (on the left). To aid the swing open the door and gently fan one pan with the hand till the desired motion is obtained. Close the door. Note three consecutive swings, say—

1.	−5	2.	+6.
3.	−4·5		

The average of the left swings is $\frac{5+4\cdot5}{2} = 4\cdot75$, therefore the centre of swing or deviation with empty pans is $+6-4\cdot75 = +1\cdot25$ or $1\frac{1}{4}$ divisions to the right. By care the student may approximately subdivide each scale division into quarters.

With a good balance the swing should diminish very slowly thus: −6,

+5; −5·75, +4·75; −5·5, +4·5, and so on. If the swing drops off suddenly, thus: −6, +5; −5, +4; −4, +3, and so on, unscrew the small bob on the pointer and raise it about half an inch. Fasten. Swing and note the effect. The swing should be slower and should drop off more gradually, the centre of gravity of the beam having been raised. The centre of swing may be slightly altered, and, if so, is brought back again by the vane as before.

These preliminaries being satisfactory, the student will now ascertain the effect of adding 1 mgm. by means of the rider in each of the four following cases:—

A_1	. .	Both pans empty.
A_2	. .	·5 gram in each pan.
A_3	. .	5 grams in each pan.
A_4	. .	50 „ „ „

A_1. *Both pans empty.*—As before, find the deviation of swing without the rider on the beam, say—

−5	+6	deviation	+1·13
−4·75			

Now, place the centigram rider on the 1 mark on the right-hand end of the beam. Note the swings, say—

−6	+5	deviation	−0·87
−5·75			

Therefore 1 mgm. causes a deviation in the swing of the pointer of ·87 + 1·13 = 2 divisions on the scale. This shows the sensitiveness of the balance unloaded. If the pointer bob be raised, the sensitiveness is increased; if lowered, it is diminished.

A_2. In each pan place ·5 gram (using, if necessary, weights from another box). Remove the rider and find the deviation. Remove the rider at the 1 mark and, as before, find the total deviation for the 1 mgm. overload. Note the results.

A_3. Proceed as in A_2, but with 5 grams in each pan.

A_4. „ „ „ A_3, „ „ 50 „ „ „

Tabulate the results thus:—

Load.	Deviation for 1 mgm. overload.
	(say) 2·0 mgms.
·5 gram	2·0 „
5 grams	1·9 „
50 „	1·8 „

The figures given throughout are imaginary, but with a good balance, through the range given, the sensitiveness should drop off but very slightly.

(*b*) **The Equality of the Arms of the Balance.**—In each pan place 50 grams. Take the deviation. Reverse the loads, placing the right hand weights in the left hand pan and the left hand in the right pan. Again take the deviation. If the arms are of equal lengths the deviations should be equal and opposite. A knowledge of the ratio of the arms is only necessary in correcting the weights when a high degree of accuracy is required (see method of checking weights given in "Ostwald"), and if weighings are made by substitution no error can result from inequality in the lengths of the arms and by the direct method of weighing; if the weights be always placed in the one pan the relative weights will be correctly given.

In the weighings just performed the student should note whether the deviation for empty pans (without the rider) is constant. It must not vary once it is adjusted. If it does so the fault generally lies in the knife edges, and can be remedied only by the maker.

B. Checking the Weights. — Various methods have been laid down for checking sets of weights. The method given by Ostwald takes into account the length of arm of the two sides of the balance. The following substitution method is convenient, simple and accurate, giving the relative values of the weights. One weight, say 0·01 gram, is assumed to be correct, and the relation of the other weights to this ascertained by counterpoising this weight placed in the right-hand pan (*r*) by a weight from another box in the left-hand pan (*l*). The ·01 weight is then removed and replaced or *substituted* by the other ·01 in the set, and its value is ascertained. The first steps are here worked out in detail, and then the whole procedure is tabulated. The set of weights here taken runs 50, 20, 10, 10, 5, 2, 1, 1, ·5, ·2, ·1, ·1·05, ·02, ·01, ·01, and the rider ·01 (*R*).

First Step.—*To check the two ·01 Weights and the Rider.*—Mark one of the ·01 weights by turning up one corner. Place it in the r.h. pan and counterprise it with a ·01 weight (from another box) in the l.h. pan. Note the deviation, which should be between +1 and − 1 if the balance was in adjustment with empty pans.

Remove the ·01 gram and replace it by the second one from the set, leaving the counterpoise in the l.h. pan. Again take the deviation. For example, suppose the deviation with the first ·01 is + 1

and with the second ·01 is + 1·25.

The second weight is lighter than the first by $\frac{\cdot 25}{2\cdot 00}$ mgm., provided an overload of 1 mgm. corresponds to 2 divisions on the pointer scale. Then the *true weights* are No. 1, ·01 = ·01 gram.

No. 2, ·01 = ·00988 gram.

Then take the ·01 gram rider and find its deviation against the same counterpoise. Suppose the deviation now is +·75. The rider then is heavier than the first ·01 weight by $\frac{\cdot 25}{2\cdot 00}$ mgm. Therfore its *true weight*, compared with No. 1, ·01 = ·01012 gram, we have now.

$$\left\{\begin{array}{l} \textit{True weight No. 1, ·01 weight} = \textit{·01 gram (assumed)} \\ \text{,,} \quad \text{,,} \quad \text{,,} \quad 2 \quad \text{,,} \quad \text{,,} = \textit{·00988 gram} \\ \text{,,} \quad \text{,,} \quad \text{,,} \quad \textit{Rider} \quad = \textit{·01012} \quad \text{,,} \end{array}\right.$$

Second Step.—*To check the two ·02 gram weights.*—Place the two ·01 weights on the r.h. pan and counterpoise with weights from the other set. Note the deviation. Remove the two ·01 weights from the r.h. pan and replace them by the ·02 gram weight. Note the deviations. Suppose with the two ·01 weights the deviation is +·5 and with the ·02 weight it is +·3 (as nearly as can be read), then the ·02 weight is heavier than the two ·01 weights by $\frac{\cdot 2}{2\cdot 00}$ mgm.

Therefore the true weight of the ·02 weight
= *·01 + ·00988 + ·0001 gram*
= *·01998 gram.*

The subsequent steps are worked out in the same way, and are indicated in the following tabulation, which, when fully worked out, will show the true values of the different weights.

Counterpoise from another Box.	Weight Tested and Substitution.	Deviation.	Difference of Deviations.	Correction.	True Weight.
·01	**·01** No. 1	+1			·01
,,	**·01** No. 2	+1·25	+ ·25	$-\frac{·25}{2·00}$ mgm.	·00988
,,	**·01** Rider	+0·75	− ·25	+ ,,	·01012
·02	·01 (No. 1) + ·01 (No. 2)	+0·5			
,,	**·02**	+0·3	− ·2	$+\frac{·2}{2·00}$ mgm.	·01998
·05	·02 + ·01 + ·01 + R				
,,	**·05**				
·1	·05 + ·02 + ·01 + ·01 + R				
,,	**·1** No. 1				
,,	**·1** No. 2				
·2	·1 + ·1				
,,	**·2**				
·5	·2 + ·1 + ·1 + ·05				
,,	+ ·02 + ·01 + ·01 + R				
	·5				
1	·5 + ·2 + ... + ·01 + R				
,,	**1** No. 1				
,,	**1** No. 2				
2	1 + 1				
,,	**2**				
5	2 + ... + R				
,,	**5**				
10	5 + ... + R				
,,	**10** No. 1				
,,	**10** No. 2				
20	10 + 10				
,,	**20**				
50	20 + ... + R				
,,	**50**				

NOTE.—To distinguish the two 1 and the two 10-gram weights, advantage must be taken of some *slight* difference in the marking or shape of the weights.

Only the details of steps I. and II. are fully tabulated. In the column "Weight Tested and Substitution" the weights substituted are in small print and weight tested in bold type. Generally the weights supplied by good makers will be found to be correct to a small fraction of a milligram, and can be used in analyses without correction. In any case the student will find the total error involved by adding up the corrected values of the weights and comparing this sum with that of the nominal values of the weights used.

General Instructions regarding the use of the Balance.

The observance of the following points will secure good results :—

1. See that the *balance* is *level* (notice the levels).
2. See that the *pans* and all parts are *clean*.
3. All *movements* must be *gentle*.
4. *Never touch* the *weights* with the *fingers*.
5. Always *place* the *weights* on the *right-hand pan*.
6. Always *use* the *arrestment* when *changing weights* or *rider*.
7. When *arresting* the *beam* the *pointer* should be about the *zero* mark on its scale.
8. Always *close* the *door* when *using* the *rider*.
9. *Never place* a *substance* directly *on* the *pan*. A watch glass or other vessel must be used.
10. *All apparatus* placed *on* a *pan* must be *absolutely clean*.
11. *Never weigh* a piece of *apparatus* when at a *much higher* or *lower temperature* than that of the *balance*.
12. Hygroscopic substances should be weighed in closed vessels.
13. *Always note* down the *weights* used *before removing* them *from* the *pan*, and check the total weight by reading the blank in the box. Remember to remove the rider.

These instructions are sufficiently comprehensive, and the student must impress them on his memory. Each instruction has its definite value, and should not be passed over superciliously as a needless refinement. Carelessness on such points, besides giving inaccurate results, will, in his future career, call for remark; an employer may safely assume that a chemist careless in weighing will be careless in other operations, and will value his services accordingly.

Methods of Weighing.—In the following instructions several methods are given for the purpose of widening the student's knowledge of the subject. Some of these methods, he will see, are unsuited to the requirements of every-day routine work where speed is an essential. The methods here taken are as follows—

A. **Determination of the Apparent Weight.**

(1) By **Direct Weighing.**

(a) By *Vibrations.*
(b) By *the Rider* (without calculation.)

(2) By **Substitution.**

B. **Determination of the Absolute Weight.**

A. (1) **The Apparent Weight by Direct Weighing.**—(*a*) **By Vibrations.**—Assuming that the weights have been checked amongst themselves as before described, and their true weights in relation to each other (relative

weights) determined, the apparent weight of any substance is obtained by counterbalancing it with these weights. No allowances are made for buoyancy of the air, nor are the weights compared with the standard of mass (a cylinder of platiniridium kept in Paris, the mass of which is called 1000 gm. or one kilogram). In all analytical operations the apparent weight only need be determined.

It is assumed as an example that the weight of a platinum crucible is required. Three operations are necessary.

1. Take the deviation with empty pans. Call this e.

2. Place the crucible on the l.h. pan. On the r.h. pan place 10 gm. Release the balance *gently*. If too light add the other 10 gm. Again release. If too heavy, remove, and try the 5 gm. in place of one of the 10 gm. weights.

If now too light add the 2 gm. weight and so on, always systematically replacing a weight that is too light by the next heavier, and one that is too heavy by the next lighter until the foil weights in the second decimal place have been used. Say the weights on the pan are $10+5+1+\cdot2+\cdot1+\cdot01 = 16\cdot31$ gms. If another ·01 is too much, place the rider on the beam and move it along systematically till equilibrium is nearly attained. Say with the rider at the 4 mark the weights are too light, and at the 5 mark too heavy. Then place the rider on the 4 mark and take the deviation. Call this deviation l (light).

3. Now place the rider on the 5 mark and again take the deviation. Call this deviation h (heavy).

The crucible weighs between 16·314 and 16·315 gms. Apparent weight then $= 16\cdot314 + \frac{l-e}{l-h}$ mgm.

Assume that e (empty pans) = +6
l (16·314) = +12
h (16·315) = −5

Apparent weight $= 16\cdot^{3}14$ gm. $+ \frac{12-6}{12+5}$ mgm.

$= 16\cdot314$ gm. $+ \frac{6}{17}$ mgm. (·35 mgm.)

$= 16\cdot31435$ gms.

Exact weighings by this method should only be made when it is certain that the object to be weighed is accurately defined down to tenths of a milligram. This case is rather rare. Vessels of glass, platinum, or other metal may change in weight whole milligrams according to the moisture in the atmosphere, therefore it is waste of time weighing to tenths of a milligram when the milligrams are doubtful.

(*b*) **By the Rider without Calculation.** — By means of the vane adjust the balance so that the pointer swings equally on both sides of the zero mark. Proceed as before to add weights to the pan till the crucible is approximately balanced. Close the door, and with the rider arm move the rider till nearly at the correct spot. Release the balance. Note the swing. If more to one side than the other, arrest and move the rider a *little* at a time, repeating till the pointer moves evenly on each side of the zero mark. Assume that the rider lies as shown in fig. 43.

Then the weight of the crucible will be 16·3140 gms., with the rider at *a*, 16·3147 gms. at *b*, and 16·3155 gms. at *c*. With practice this operation

can be very quickly performed, the left hand working the milled head and the right hand the rider arm.

This method is sufficiently accurate for all the work in this section, and will be found the most convenient and rapid. When performing a series of weighings the balance should be checked every now and then to see that the pointer swings evenly on each side of the centre. When noting down the weights add them up mentally as follows:—(10 + 5 + 1 = 16), (·2 + ·1 = ·3), (·01), (Rider ·42), total 16·3142. Also when returning the weights to the box add up mentally the empty spaces as a check on the former addition.

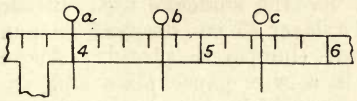


FIG. 43.

A. (2) **Weighing by substitution.**—The previous methods give good results provided the balance (as is generally the case with good makers) be well designed. In the method to be described good results may be obtained even with a very inferior balance.

Place the crucible (or other object to be weighed) on the l.h. pan. On the right-hand pan place a watch glass, and with a small spatula place on it some litharge (or other heavy powder), adding or deducting a little at a time till the crucible is approximately counterpoised. Obtain exact equilibrium by a rider on the right-hand end of the beam. Now remove the crucible and in its place put weights from the box till equilibrium is again obtained, using a rider on the left-hand end of the beam.

Note the weights thus used. Then if these weights are correct (or are checked as before by substitution) the true apparent weight is thus obtained.

B. **Determination of the Absolute Weight.** — For fine weighings such as are required in certain physical measurements allowances are made for the different densities of the various weights and the substance weighed. The weights again have to be checked, not only amongst themselves, but also must be compared with the standard of mass. For this purpose it may be taken that 1 cubic decimetre of water at 4° C. weighs 1000·013 gms. As these matters relate more to Physics than Chemistry the student is referred to *Elementary Practical Physics*, by Stewart and Gee.

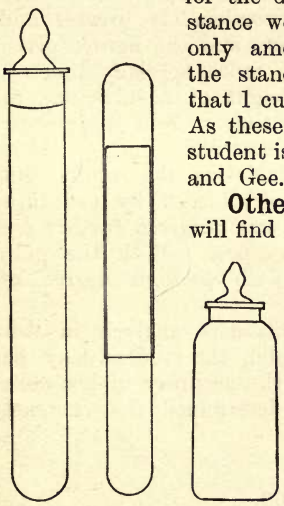


FIG. 44.

Other Apparatus used in Weighing.—The student will find it convenient to procure or prepare a pair of counterpoised watch glasses about 6 cm. in diameter; or he may take a single watch glass and prepare a counterpoise from a piece of brass by filing. If accurate within a milligram, the final adjustment may be made with the rider. When required to weigh out some quantity of a powder he places the

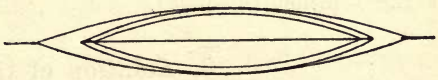


FIG. 45.

watch glass on the l.h. pan and the counterpoise on the r.h. pan. Then with a spatula or from any vessel he adds to the watch glass some of the powder and ascertains its weight. Special care must be taken that none of the powder falls on the pan.

Fig 44 and fig. 45 show three forms of weighing bottles and a pair of

watch glasses in a clip. These are used for hygroscopic substances (which absorb moisture from the air and will be referred to further on).

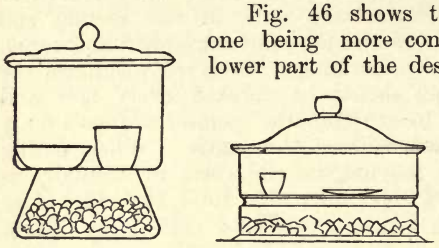


Fig. 46.

Fig. 46 shows two forms of desiccators, the left-hand one being more convenient for the student's use. In the lower part of the desiccator a layer (3 cm. deep) of calcium chloride (lumps) is placed. Above this is a wire gauze plate and triangle on which rest the articles to be desiccated or dried. The joint of the cover and body is accurately ground, and should be *neatly* smeared with vaseline. The calcium chloride being a strong absorbent of moisture, rapidly dries any article placed on the gauze, and as the lid is air-tight, moisture cannot enter from the outside atmosphere.

The Quantity of Material to be Weighed out. — This is generally based on the quantity (supposed to be present) of the substance sought. Where this is approximately known ·3 to ·5 gm. will be sufficient if the substance sought is present in fairly large proportion, say over 20 or 30 per cent. If only a few per cent., then 2 or 3 gms., and if fractions of a per cent. 5 gms. or more.

This, of course, presupposes knowledge that the student frequently does not possess. If, then, he has nothing whatever to guide him, let him take about 1 gm. and run a trial. Then, if he finds only traces of the substance sought, he must take a larger quantity, say 5 gms., or if he finds a high percentage he may take ·3 to ·5 gm. He must so regulate the quantity that the precipitates obtained are not too bulky. A large precipitate is difficult to wash, dry, and ignite, and again, on the other hand, with a very small precipitate the manipulation losses are proportionately greater and cause serious error. The happy mean must be struck, and the figures given afford some clue as to the right proportions. Never, unless specially directed, weigh out *exactly* 1 gm. or ·5 gm. or other exact weight of a substance, as the final adjustment of such a weighing takes much time. Add the powder approximately, and then ascertain the weight taken, say ·9982 gm. or ·5120 gm., etc. This involves a little extra time in calculating the results, but with the aid of logarithms this is more than counterbalanced by the time saved in weighing. Examples of these calculations will be given further on. These remarks only apply to the delicate chemical balance. With the pulp scales large quantities can be weighed exactly with a high degree of accuracy.

In some of the preliminary exercises in quantitative analysis in this section, instead of taking a weighed quantity of a solid, the student may be given a certain volume of a checked solution, and the accuracy of his work is checked by the demonstrator, who has carefully determined the contents of the solution (in bulk).

3. Solution of the Substance.

Material of Vessels for Solution.—The student must consider the effect of the solvent used on the vessel. In most cases the solvent used is an acid or mixture of acids, and for such solvents glass and porcelain are generally used. Platinum may be used, provided no chlorine or other attacking agent be present. (See notes regarding care and use of platinum crucibles.) For strong alkalies silver or nickel vessels should be used, as glass is attacked sensibly by hot and

even cold solutions of caustic potash or soda, and porcelain is also attacked to some extent.

Methods of Solution and Apparatus used.—When a substance is soluble in water and the solution does not require boiling, place the substance in a glass beaker, as at *a* in fig. 47. Add the water. Cover the beaker with a clock glass and heat. The solution may be boiled, but in this case it is better to perform the solution and boiling in an Erlenmeyer flask, as in fig. 47 at *c*.

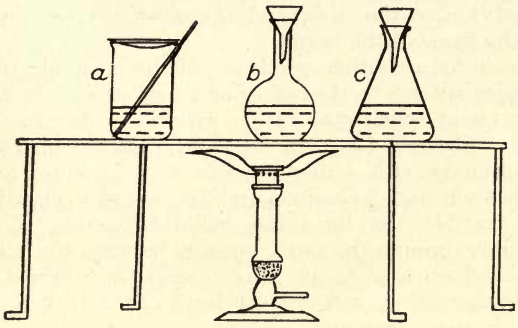


FIG. 47.

A funnel is placed in the mouth of the flask and through it the water is poured, whilst at the same time it serves for a cover. Or, again, the flask inclined will serve the same purpose. Where effervescence takes place on solution these methods serve to prevent mechanical loss through small globules of the liquid being projected over the edge.

If required, solution may be performed in a porcelain dish with an inverted funnel of smaller diameter than the dish, fig. 48, or a cover or a casserole (a deep porcelain dish with a lid and handle) may be used.

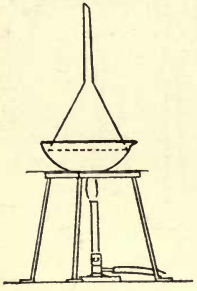


FIG. 48.

In most laboratories, as gas is available, heat can be applied by placing the vessel, after drying the outside, on a piece of wire gauze on an iron tripod about 8 inches high. The wire gauze may be replaced by a piece of thin asbestos board or a piece of wire gauze felted in the centre with abestos. The bunsen burner is then placed underneath and lighted, the colourless flame always being used. The Argand burner is shown in fig. 49.

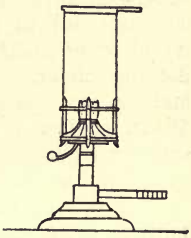


FIG. 49.

Where much work is to be done, an iron plate (30 cm. × 25 cm. × 4 mm.) mounted on a four-legged stand is very convenient. If its surface is kept clean and glass vessels are wiped before transference to the hot plate, there is little danger of breakage. A few squares of thin asbestos board (about 10 cm. square) are useful for placing under a vessel to reduce the temperature. Sand baths are sometimes recommended, but the iron plate, with or without asbestos board or cloth, is a neater arrangement, and with a large bunsen (Fletcher Russell) gives a good range of temperatures. See fig. 47.

After solution, evaporation is frequently required. This may be carried out as shown in fig. 18, p. 7, the solution being transferred to the porcelain evaporating dish by pouring down a glass rod and washing the vessel and rod with a jet from the wash bottle. The beaker and porcelain, arranged as in fig. 50 *a*, are then placed on the hot plate, and the steam from the boiling water in the beaker heats the dish and slowly evaporates the solution.

In fig. 50 *b* and *c* are shown the elevation and plan of a self-filling copper water bath. Water is led in at the side and out at the bottom tube, and a con-

stant level is maintained in the bath. The series of rings permits of considerable variation in the size of evaporating dish.

With care and practice evaporation may be carried out on the hot plate or tripod and gauze. The solution should never be allowed to actually boil; and towards the end of the evaporation, when the concentrated solution is liable to spit, a piece of asbestos board is placed under the dish, and the heat lowered by turning down the flame of the burner.

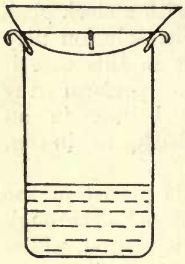


FIG. 50 *a*.

Certain substances are either partly or wholly insoluble in acids, and require special treatment prior to solution. As a rule, such treatment consists of fusion with some flux in a metal crucible. Silicates, for instance, are intimately mixed (when finely ground) with either carbonate of sodium or carbonates of sodium and potassium, and the mixture placed in a platinum crucible, the lid being inclined so that the contents are visible through the small opening between the lid and crucible. The crucible is placed on a platinum wire triangle on a tripod, and heat is applied by a bunsen burner till the charge just begins to melt round the edges. The foot blowpipe is then brought into position, the flame being turned on gradually till the whole mass is in a molten state. Care must be taken that the mass does not boil over. This may be prevented by carefully watching the contents through the opening and regulating the blast flame accordingly. This operation, unless otherwise directed, must be continued till the contents are in a state of tranquil fusion, and no blebs of solid or semi-solid matter are seen floating about. The flame is now turned out, and the crucible and contents are allowed to cool. When cool, the crucible, contents, and lid are transferred to a beaker. Distilled water is then added and a few c.cs. of hydrochloric acid. The beaker and contents are then gently warmed till solution is complete, when the crucible and lid are raised up with a glass rod and washed with a jet of hot water from the wash bottle.

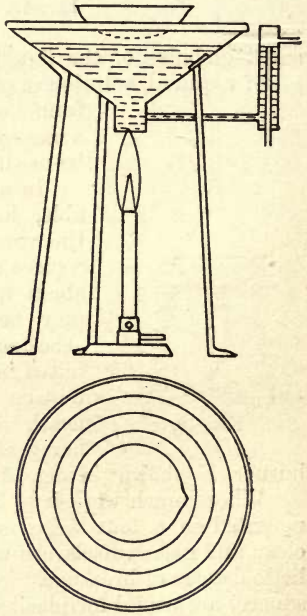


FIG. 50 *b* and *c*.

It will be seen in this case that by fusion the insoluble silica or silicate is changed into soluble silicates of sodium and potassium. As such a fusion takes from fifteen to thirty minutes with the foot blowpipe (see fig 51), this work will be found somewhat tedious, and where many fusions or ignitions with the blast have to be performed, it is advisable to replace the foot blower by a water blast. This piece of apparatus, in a very compact form, and suitable for both blast and suction, can be procured at a very moderate figure, and is easily attachable to the water service above a sink, the connection being made with lead or compo piping. This apparatus will serve for many purposes—ignition, fusion, filtration, glass-blowing, as an aspirator, etc.; and though rather expensive if provided for each student, one on every working bench can be recommended. Instructions regarding its manipulation are issued by the makers.

In fusion, as in solution, the effect of the flux (solvent) on the crucible

must be considered. As a rule, porcelain crucibles are of little use, as the glaze is readily attacked, more especially by alkaline fluxes.

When using platinum crucibles certain precautions must be observed. The following are some of the chief:—

1. Platinum is attacked by **free chlorine**, therefore it must never be used as a containing vessel for any mixture yielding free chlorine. Under certain conditions $KClO_3$ will yield free chlorine. Similar remarks apply to **bromine** and **iodine**. Again, chlorides and nitrates in the presence of H_2SO_4 are liable to yield free chlorine.

2. Compounds of **silver, lead, tin, bismuth, antimony,** and **arsenic** should under no circumstances be either ignited or fused in platinum vessels. Most of these metals have a low melting point, and when reduced from their compounds they readily alloy with platinum, and a probable result is that the bottom may be melted out of the crucible—that is, the destruction of a piece of apparatus worth from £3 to £6. In such cases porcelain crucibles should be used.

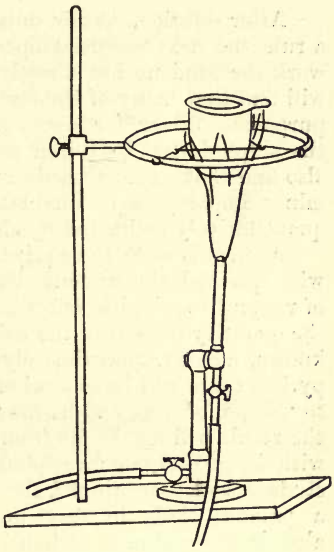


Fig. 51.

3. Where **caustic soda** or **potash** or **barium oxide** is used as a flux, platinum vessels should never be used. To this might be added **sodium peroxide**, as, if impure, it frequently attacks platinum. In such cases silver or nickel vessels should be used.

4. After a platinum vessel has been used for fusion or ignition, clean it by rubbing in the hollow of the hand with the fingers and a little sea sand the grains of which, under a lens, all appear rounded. For accurate work the surface must be kept in a bright state. **Sharp sand** must be avoided, as it scratches the surface of the vessel. Stains may be removed by fusion with $KHSO_4$.

5. When igniting or fusing, the vessel should always be supported on a triangle of platinum wire. This triangle may be made cheaply by running a thin platinum wire from the middle points of the sides of an iron triangle with sides about 7 to 10 cm. long. (Platinum foil wrapped round a pipe-clay triangle will answer.)

6. A **bad gas supply** is liable to be the cause of a grey frosting on the outer surface of the vessel. Only the outer non-luminous cone of the bunsen or blast flame should be used. Here the student is at the mercy of the gas company unless muffle furnaces are available. If a fusion be conducted in the muffle, any loose bone ash should be cleared away, and a small square of asbestos board inserted, on which the crucible is placed. When the fusion is complete, the board and crucible are gradually and carefully removed by the aid of a pair of cupel tongs.

7. The student taking a course in metallurgical chemistry should possess his own crucible. Though expensive, it is always a valuable asset.

Saturated solutions.—In the course of his work the student may require a saturated solution of some salt. Take a 200 c.c. Erlenmeyer or ordinary glass flask. Select a good cork, and through it fit two glass tubes, each bent at a right angle, one passing 3 cm. through the cork, and the other nearly to the bottom of the flask and slightly contracted at its lower end. Fill

the flask about two-thirds full of distilled water. Add an excess of the coarsely powdered salt; insert the cork and fittings. Connect the shorter tube to an aspirator or the longer tube to the blast, and pass a steady current of air through the solution. If necessary, the solution may be aided by placing on a tripod and asbestos board and applying heat by a bunsen burner.

The same end may be obtained, but much more slowly, by ordinary methods, aided by shaking.

4. PRECIPITATION.

After solution, certain minor operations may or may not be necessary, but as a rule the next essential operation is that of precipitation. In his qualitative work the student has already come across many cases of precipitation, and he will find that many of the methods there used are again applied for quantitative purposes. Silver, for instance, is precipitated as the chloride **AgCl**, copper as the sulphide by H_2S, iron as the hydroxide by NH_4HO, and so on. He will also find that some methods are introduced which are either not used or are of minor importance in qualitative work. Copper, nickel and other metals are quantitatively estimated by electrolysis.

As in this work the equivalent system of reagents is employed unless otherwise specified, the student may in every case calculate very closely the amount of reagent required to effect complete precipitation in a given case if he knows the quantity present of the substance to be precipitated. Even where this is not known, he may approximately estimate, for instance, that in half a gram of iron pyrites there will be somewhere between 40% and 50% of iron, that is, about ·2 to ·25 gm. of iron, and he may then proportion his precipitant accordingly, and the result will not be far from that desired. The habit of drowning the analysis with large doses of precipitant must be carefully avoided, not because, as the student sometimes thinks, the authorities grudge him materials, but because such a practice leads to very uncertain results. There are sufficient difficulties already in existence without increasing them by adding variable quantities of precipitant. In every precipitation there is a certain point, more or less definite, at which the best precipitation is attained. It is not claimed that this point is exactly known in all cases, or even in the majority of cases, but the instructions given in the following pages will in all cases at least give an approximation to the desired end—an approximation giving sufficiently accurate results for the purposes of the chemist employing gravimetric methods.

As the methods of gravimetric analysis are more and more investigated, the conditions securing accuracy become more defined; points of doubt are cleared up and the science becomes more exact. To benefit by the results of such research the student must have access to the current chemical literature; and whenever a criticism or research connected with his work appears, he should note its bearing and claims, and if possible try any variations or innovations suggested, bearing in mind that a new method must be viewed with caution, and must not be adopted till its claims are proved (personally) to be true.

In precipitation the following two main conditions should be aimed at:—

(*a*) The precipitation should be as complete as possible.

(*b*) The precipitate should be obtained in the best possible condition for easy filtration and thorough washing.

Regarding completeness of precipitation, something has already been stated in the Qualitative Section. Here it is even more important than there. The point at which precipitation is complete is rather difficult to determine in some cases.

Generally the calculated quantity may be added, and one or two c.cs. allowed in addition. A test may be made of the supernatant liquid, or by filtering a small portion and testing the filtrate. The student must bring all his chemical knowledge to bear in ascertaining the completeness of precipitation, and must always apply tests to check the operation, that is, to ascertain whether too little or too much of the precipitant has been added.

Regarding the physical condition of the precipitate it is impossible to generalise, and whenever necessary, special instructions will be given. Frequently, though not always, precipitates thrown down in hot to boiling solutions, with the gradual addition of the precipitating solution, aided by continual stirring, produce the best results.

The precipitating reagent should always be added, unless otherwise specified, in the liquid form, or where a gas is the precipitating agent, it should be passed through the liquid, and in this case again heat frequently aids precipitation. Care must be taken that the gas is purified in a suitable wash bottle before passing through the liquid. The gas delivery tube should be drawn to a point about 2 mm. in diameter, and in certain cases slight pressure is beneficial, and may be obtained by precipitating in a flask, through the cork of which the gas delivery is led and a small exit tube is fitted, drawn to a fine point. Care should be taken that all the precipitate attached to the gas tube is removed. Further instructions will be given where needed in the details of methods given in the following pages. No special notes need be given regarding the vessels used for precipitation. For the generation of H_2S, CO_2, etc., Kipp's Generator will be found convenient.

5. FILTRATION.

When precipitation is complete the precipitate must be separated from the solution. The means of bringing about this separation will be described under this head. Under the next head (6. *Washing*) the completeness of this separation will be considered.

(*a*) **The Filtering Medium.**—In quantitative gravimetric analysis the two materials generally used are paper and asbestos, and the student must be familiar with the use of both of these. He has already used paper in his qualitative work, but in quantitative analysis paper of a special quality must be used. This paper in various qualities may be obtained from the dealers. It is usually put up in packets of 100 pieces of circular shape. The most convenient sizes are 9 cm. and 11 cm. in diameter. As these papers are frequently incinerated along with precipitates, it is obvious that any ash resulting from the incineration of the paper must be allowed for. The amount of ash in each paper is generally stated on the cover of the packet, but this should be confirmed by the method given under "Ignition." For the present it will be assumed that the student has procured two packets of papers of the quality and size mentioned.

Papers of the sizes mentioned should not yield more than one milligram of ash. Papers specially treated with hydrochloric and hydrofluoric acids may be obtained. In these the ash which is less than ·0003 gm. may be disregarded. If time permits, the student may prepare these papers. Papers of 7 cm. diameter will be found convenient if very small precipitates have to be filtered, or if the bulk of the filtrate has to be kept as small as possible. A small paper can be washed with less solution than a large one. Besides paper, the chief filtering medium in extensive use is asbestos. This in conjunction with the Gooch crucible gives the most convenient, accurate, and rapid method known of filtering many precipitates. Paper consists

largely of carbon, which on incineration passes away as CO_2, leaving a small quantity of ash behind. Asbestos, on the other hand, when properly prepared and incinerated, suffers no loss. When, as in the Gooch method (see Methods of Filtration), a precipitate is separated on a thin layer of asbestos, it may then, without additional handling, be dried and incinerated or it may be dissolved even by strong acids. In his future work the student will see that in many cases, both as regards accuracy and convenience, asbestos is preferable to paper.

In order that asbestos may give accurate results, it must be unacted on by the acid or other substances present in the solution and subsequent washings, and must suffer no loss on ignition. The asbestos chosen should be of a soft silky fibre. A little is taken in the fingers and carefully *scraped* down with a knife into very fine soft down. Continue the process till sufficient is obtained for a number of filtrations. Transfer the fine asbestos to a glass beaker, add strong **HCl**, and boil for half an hour or longer. Decant the greater portion of the acid, add distilled water, and transfer the contents of the beaker to a large filter (either of paper or the platinum cone). The asbestos is then thoroughly washed, then dried in the air oven and transferred to a bottle for safe-keeping. The preparation of the filtering surface will be described under the Gooch method of filtration.

(*b*) **Methods of Filtration.**—In analytical work the separation of the precipitate from the solution is effected by passing the solution through some medium the pores of which are sufficiently fine to obstruct the passage of particles of the precipitate. Generally the solution passes through from above, and the weight of solution above the filter causes the solution to run through. The rate of filtration may be much increased by the use of a vacuum underneath the filter, which may be either paper or asbestos. The student must be proficient in both methods.

1. **Filtration unaided by a vacuum.** — This method has frequently been used by the student, and the necessary apparatus is by this time quite familiar to him. It may happen that in his qualitative work the student has acquired careless habits. If, on reading the following, he finds that his practice does not coincide with the details laid down, he must reform his ways. It is only by continuous attention to details that the skill in manipulation which marks a good chemist can be secured.

The necessary apparatus is shown in fig. 16, p. 6, and consists of beakers, funnels and stand, glass rod and filter papers.

Carefully fold one of the papers twice at right angles, as shown in fig. 15, p. 5. Place it in a funnel (sides sloping at 60°), carefully opening out and pressing the paper to the glass. Place the funnel and paper on the stand. Place a beaker under the funnel and adjust its height so that the tip of the stem touches the edge of the beaker near the top, so that the filtrate may run quietly through and not splash. Now carefully spray the paper with hot distilled water from the wash bottle. Take the beaker with the precipitate to be filtered in the right hand and the glass rod in the left, and held at its upper end in the tips of the fingers and thumb. Bring the lower end within half an inch of the filter paper near the point, and carefully pour the liquid down the glass rod by bringing the lip of the beaker in contact with the rod. The solution is run in till 1 or 2 cm. from the top. Remove the beaker, letting any drop on the lip of the beaker run down the rod (not the outside of the beaker) into the filter. When the bulk of the liquid has filtered through, the funnel is replenished and the process repeated till the contents of the beaker have been transferred to the filter. The final stage of this transference is effected by the wash bottle, the beaker

being nearly inverted, with its lip over the filter, and the jet of the wash bottle at the same time directed with the finger upwards into the inverted beaker, and any adhering precipitate is washed down on to the filter. If the precipitate is to be washed by decantation (see Washing), it is not at this stage transferred to the filter paper. The method described is that generally adopted where paper is used as the filtering medium. It answers well with substances that filter easily and do not choke the pores of the paper, but with many substances it leaves much to be desired as regards time.

2. **Filtration accelerated by a vacuum.**—As has just been mentioned, filtration becomes prolonged and tedious in certain cases, and any means of cutting down the time is of value both to the student and the practising chemist. The usual method of accelerating filtration is by the application of an exhaust, that is, by the creation of a vacuum on the under side of the paper or other medium. The means of creating this vacuum and connecting it to the filter will first be considered, then the methods of accelerated filtration through paper and asbestos. Where a water supply at a fair pressure is available, the most convenient method of obtaining an exhaust is by what is termed a filter pump. This is simply a small injector, working on the same principle as the boiler injector (steam). The water, under pressure from the tap, forcing its way through the conical jet opening, forms a vacuum, and the air is sucked in at the side. If rubber connections are used, they must be firmly bound and wound with copper wire. Metal connections are preferable, though rubber will do. A rubber tube is connected to the side tube, and at the other end to a flask or Woulff's bottle, as shown in fig. 52. This prevents any water, running back from the pump (on turning off the suction), from running into the filtrate.

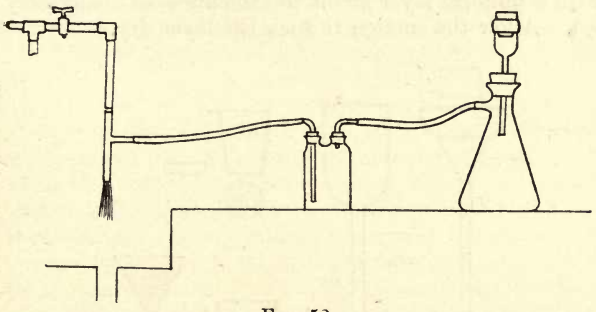


FIG. 52.

Whenever the aid of the vacuum is required, a connection is made between the Woulff's bottle and the filtering apparatus, which is shown on the right hand in the sketch.

(*a*) **Accelerated Filtration through Paper.**—Unless strengthened, the usual filter paper is rather too weak to stand the extra pressure caused by the suction, therefore a small platinum cone, thickly pierced with small holes, bored from the inside outwards, is used in the apex of the funnel. This cone may be made from platinum foil. The cone is dropped into the point of the funnel; then the paper is fitted in; the funnel stem is passed through a cork which fits the mouth of the filter flask. The cork and funnel are firmly fixed in the filter flask, and its side branch is connected to the Woulff's bottle. Fill the funnel with water, and start the pump to see that everything is in working order. If so, empty the water out of the flask and then commence filtration, always keeping the funnel well filled with the liquid. The exhaust should always be turned on gradually, and worked up to its full capacity only when necessary. The filter flask may be conveniently replaced by a separating funnel if it is desired to draw off the filtrate during the process.

(*b*) **Accelerated Filtration through Asbestos—The Gooch Crucible and the Platinum Cone.**—The preparation of the asbestos fibre has been described.

The necessary apparatus and method of filtration will now be taken. The crucibles used are shown in fig. 53.

They may be made either of porcelain or platinum. Platinum is more satisfactory, but more expensive. The bottom of the crucible is pierced by a large number of fine holes. The crucible is fitted into the glass funnel (see fig. 53) by a rubber joint consisting of a 5 cm. length of wide bore, thin walled, rubber tubing. An air-tight joint is thus secured. The funnel stem passes into the filter flask as usual, and the usual arrangements connect the filter to the exhaust. The platinum cone shown may be used in a funnel, the subsequent operations being the same as those with the crucible, except that the cone cannot be used for ignitions. Having now connected up the apparatus, the asbestos filter must be prepared. Take from the bottle a *little* of the asbestos, place it in a beaker, and stir it up with 50 to 100 c.cs. distilled water; pour slowly into the crucible and turn on the exhaust. Continue pouring in the solution down a glass rod, the tip of which is kept near the bottom of the crucible. A fine coat of asbestos gradually forms. A little more asbestos is added in the same manner till a uniform layer about the thickness of moderately stout filter paper is obtained. Allow the suction to suck the layer dry.

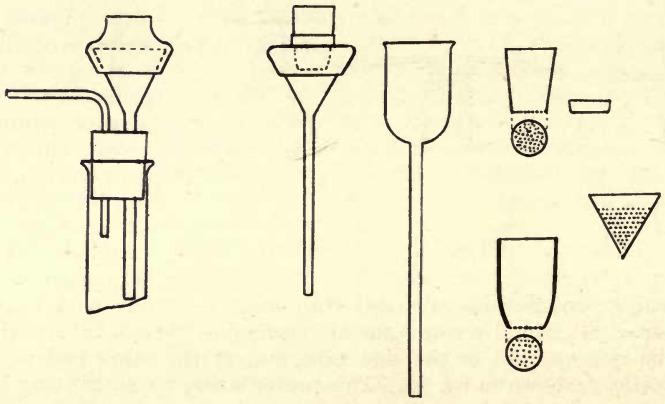


FIG. 53.

The crucible is now ready for filtration, but as it will also be used for ignition and weighing of the precipitate, it is now removed. Any fibres adhering to the bottom are removed and the small cap is slipped on. (These caps may be procured in platinum for porcelain crucibles, and are an advantage in incineration.) The crucible is now dried in the water oven, then incinerated and weighed (see following headings). The cap is now removed and the crucible replaced in the funnel, and filtration commenced by gently pouring the solution down a glass rod, the tip of which is brought close to the asbestos. The vacuum is then applied as usual.

This method of filtration is specially applicable when the precipitate is to be ignited. It is also of much value when a precipitate is to be dried and weighed without ignition. The method of weighing such a precipitate on counterpoised or weighed filter papers is inaccurate, and should always be replaced by the Gooch method.

The necessary apparatus is cheap if a porcelain crucible be used. A small thin platinum cap is cheap, and may be slipped on the porcelain during ignition, though the ignition may be performed without this device.

6. WASHING THE PRECIPITATE.

A precipitate may be washed directly on the filter, or it may be washed partly by decantation and partly on the filter. If by decantation, the precipitate is allowed to settle, and the supernatant liquid is poured on the filter. Wash water is added to the precipitate, and after settling, the decantation is repeated a few times, and finally the precipitate is transferred to the paper or Gooch crucible.

Whatever method of washing be used, it must be thorough; and that this may be so, both the precipitate and the paper or asbestos must be washed free from all traces of the original solution. This must be ascertained by careful tests; guesswork on the 'good enough' principle is the sure road to inaccuracy, and must never be permitted. It may appear that the chemist sometimes guesses at the completeness of a washing. This is not so, as when he does not apply a test he knows from experience gained in many analyses that, say, four washings serve to remove certain salts. The student must likewise gain experience by continually applying tests; and it is only in routine work, where hundreds of analyses of a kind are performed, that it is at all justifiable to omit tests.

For practice, let the student place a paper in the funnel and thoroughly moisten it with E. H_2SO_4; then let him wash it by a jet of hot water, applied first at the upper edge and then downwards to the point, till the paper is over half filled with water. Let this drain. Repeat the washing three times. Dry the funnel and paper in the air bath at 110° C. Then cautiously increase the temperature. If any H_2SO_4 remains in the paper a black stain appears. This forms a good check on his manipulation. The general failing of students is to neglect the top edge of the paper. The results can also be checked in a repetition of the experiment by testing every now and then about 1 c.c. of the washings caught in a test tube with a little $BaCl_2$ solution.

Unless otherwise directed, hot water should be used for washing; and as a rule, when using filter paper, each washing should drain through before applying another. In this way a smaller quantity of water will do the required work. This is of importance, as, when the filtrate is to be further treated, a large bulk is objectionable. When the Gooch method is used, the washing water is added before the crucible is drained, a little liquid being kept above the filter till the final wash, when the crucible is drained.

Particles of precipitate adhering to a beaker may be removed by rubbing with a piece of rubber tubing on the end of a glass rod.

In testing the completeness of a washing, the most delicate qualitative tests must be applied. The student should now be in a position to apply these tests intelligently. If the filtrate is reserved for further treatment, tests should not be applied till about the third wash, as a certain quantity of the filtrate is thus lost.

If a chloride and a nitrate be present in the solution it will be safe to test the washings for chlorine alone, and assume that if the chloride is washed out, the nitrate has also been removed, as its solubility is not far removed from that of the chloride. This assumption is further justified, in that the qualitative tests for chlorides are more delicate than those for nitrates.

When applying the jet from the wash bottle a gentle pressure from the mouth on the water in the bottle must be maintained, and care must be taken that the precipitate is not splashed up the sides of the glass funnel, or that the layer of asbestos in the Gooch crucible is not disturbed. The jet should not be directed on the precipitate till a steady stream has been

obtained. A small stop valve ground into the bottom of the delivery tube, as shown in fig. 54, may not be beyond the student's capabilities in glass working, and serves to maintain a column of water in the delivery tube, and prevent the first portion coming through the jet from splashing the precipitate.

7. DRYING AND IGNITING THE PRECIPITATE.

After the precipitate has been separated from the solution, it has in some cases to be dried and then weighed; in others, it has to be dried and ignited before weighing. The operations of drying and ignition and the necessary apparatus will now be described.

(*a*) **The Apparatus required.**—Precipitates are generally dried in water or air ovens. When the drying temperature is not to exceed 100° C. the water oven is used, and when over 100° C. the air oven. The actual temperature of the precipitate in the water oven rarely, if ever, reaches 100° C. under normal conditions; and when instructed to dry a precipitate in the water oven at 100° C., it will be sufficient to heat the water to the boiling point and transfer the precipitate to the oven. If specially desired, the boiling point of the liquid in the jacket may be raised by adding a little salt to the water.

The water oven itself is shown in fig. 55, and is made of copper. It consists of a chamber with one or more shelves perforated with holes. This chamber is provided with a door at the front, and on all sides, except the front, is surrounded with water contained in an outer chamber or jacket. The top of the oven shown is adapted for evaporations, and at the side is a constant level feed for the water supply. A cork, carrying a thermometer to indicate the temperature, is inserted in an opening provided on the top of the oven. The thermometer bulb should come well down to the centre of the inner chamber. The water oven may be connected with a condenser, and a supply of distilled water is thus economically procured.

FIG. 54.

When a precipitate is to be dried on a paper, the funnel and paper are transferred to the oven, the stem of the funnel being passed through one of the holes in the shelf, and the top of the funnel is loosely covered with a piece of filter paper to prevent contamination by dust, etc., or the filter may be removed from the funnel and set on its side on a large watch glass. The burner under the oven is lighted and heat applied till the precipitate is apparently dry and no more vapour is seen rising from its surface. The door is closed during drying, and is only opened for removal or inspection.

The operation of drying may also be carried out conveniently and quickly in the air oven, provided the temperature be carefully regulated. By a little experience the student will be able to control the temperature of the oven within a few degrees of the required point by adjusting the bunsen flame, but, for more accurate work, a gas regulator (so called Thermostat) should be fitted to the oven.

The oven is made of stout sheet copper, in the form of a cubical box with a door on the front. The door has a small shutter for admission of air. Inside is a shelf about 4 cm. from the bottom of the oven, and another shelf may be inserted, if required, higher up. The oven rests on a four-legged stand, and is heated by a bunsen burner. In the top of the

oven are two holes, one for the thermometer and the other for the gas regulator. It is advisable to cut a V-shaped notch along the cork carrying the thermometer, as this permits the easy escape of vapour. The oven, with the thermometer and gas regulator in position, showing the connection to the gas supply, is seen in fig. 56.

The gas regulator is made of glass; the long thermometer-like tube and the first cross arm are filled with mercury. In this cross arm is a screw which can advance or retreat, and force the mercury up or down the tube. The gas is led through the regulator as shown, and when the temperature exceeds a certain point the mercury in the tube rising shuts off part of the gas and thus lowers the bunsen flame. By adjusting the screw and the quantity of mercury, the temperature may be kept constant at any desired point. For convenience, the student may regulate the temperature to 110° C. A little alteration of the screw inwards or outwards will set the regulator at any other temperatures required.

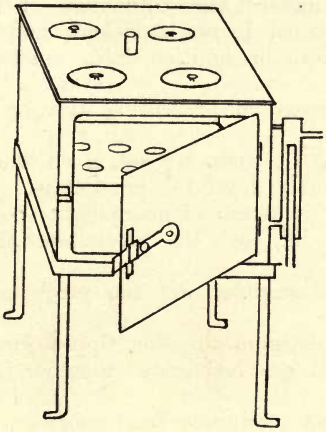


FIG. 55.

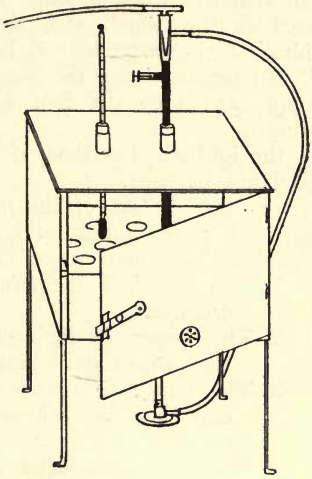


FIG. 56.

The thermometer bulb should come within an inch of the lower shelf if the substance to be dried is placed on that shelf. If a funnel and contents are to be dried a middle shelf should be used, the stem going through one of the holes in the shelf. When the temperature is of importance an article should not be set directly on the lower shelf, as it is usually somewhat hotter than indicated by the thermometer. A square of asbestos board is convenient when placed on the lower shelf, as substances may be dried upon it without danger of overheating.

Precipitates in the Gooch crucible are dried in the same way. Care should be taken that the shelves on which the crucible is placed are perfectly clean, and that the roof of the oven has no hanging scale which may fall into the precipitate.

After drying, the precipitate frequently has to be ignited, that is, heated to a dull or a bright red heat, either in the air or in a current of some gas such as hydrogen, carbon dioxide, coal gas, or oxygen.

When paper has been used for the filtration, this as well as the precipitate must be incinerated. The necessary apparatus will be shown in the following illustrations, and consists of a bunsen burner, an iron tripod about

20 cm. high, a pipe clay triangle for porcelain crucibles, and a platinum wire triangle for the platinum crucible, a glass stirring rod with rounded end (or a stout platinum wire), porcelain crucibles and lids (about 2·5 cm. in diameter by 2·5 cm. deep), and if possible a platinum crucible and lid (weight about 20 gms. to 30 gms., cost £3 to £4, 10s.), crucible tongs.

Methods of Incineration.—When the reducing action of the carbon will have no action on the precipitate, the paper and precipitate are first dried and then are placed in the crucible, which is set in the triangle on the tripod. The crucible is tilted at an angle of about 45° and the bunsen flame is gently applied—at first by taking the burner in the hand and moving the flame across the bottom of the crucible. The paper takes fire and burns, leaving a black mass. The burner is now set under the crucible so that the flame strikes the bottom, and the heat is increased and the ignition continued, with occasional careful stirring by the glass rod or platinum wire, till all black particles disappear. The crucible is then removed with the crucible tongs and placed in the desiccator, the tongs being replaced on the bench with their *points* up. The preliminary ignition and weighing of the crucible will be described under "The Estimation of Filter Ash." In certain cases the heat of the bunsen is not sufficient, and must be supplemented by the foot blowpipe (blast) or ignition in a muffle (see Assaying).

In the ignition described, if care is exercised in preventing draughts, the lid need not be used.

Where the carbon of the paper will have a reducing action on the precipitate, the paper must be ignited separately from the precipitate. This may be done in several ways, differing only in detail of manipulation :—

1. The paper is incinerated on the lid, and the precipitate in the crucible.
2. The paper is incinerated in the crucible, and the precipitate is then added and incinerated.
3. The paper is incinerated on a platinum wire (or tipped forceps), and then the ash and precipitate are incinerated together in the crucible.

To prevent loss when separating the dried precipitate from the paper, the student should procure a number of pieces of glazed paper (preferably black) about 15 cm. × 22 cm. A piece of this paper is placed on the clean bench, and by gentle squeezing and shaking the precipitate is, for example in the third method mentioned, transferred to the crucible which has been placed on the glazed paper. Any precipitate falling outside the crucible is caught on the glazed paper. The filter paper is opened out, and by gently rubbing the interior surfaces against one another most of the remainder of the precipitate is removed. Fold up the paper and wrap round it a few turns of a platinum wire mounted in a glass tube or rod. Take the rod in the right hand so that the paper is about two inches above the crucible, and in the left hand take a bunsen burner and kindle the paper, as shown in fig. 57. When the paper ignites, remove the bunsen flame, and the charred remains glow till the carbon is all burnt away. By a gentle tap the skeleton of ash falls into the crucible. Any particles of precipitate or ash on the glazed paper are now transferred to the crucible, which is placed on another piece of glazed paper, the former piece being doubled scoop-like, and the particles brushed down with a small camel's-hair brush, care being taken that no small particles are left entangled in the hairs of the brush. The crucible and contents are then ignited over the bunsen or blast flame as may be required.

In the first and second methods mentioned the details are obvious, the precipitate in the second method being transferred to a piece of glazed paper, and covered with an inverted glass filter funnel whilst the ignition of the paper proceeds.

The superiority of the Gooch methods is now very evident. There is no separation of filter and precipitate; and after drying, the precipitate is ready for incineration. The cap is slipped on and the crucible set on the triangle and the ignition commenced at a low heat, gradually raising the temperature till the incineration is complete. If the porcelain Gooch crucible is not provided with a cap, care must be taken when incinerating that particles of the filter or precipitate do not get detached. As every additional handling increases the probability of error, it is seen that, besides mere saving of time, the Gooch method may justly claim a higher degree of accuracy than the paper method; and where precipitates are acted on by the carbon of the paper, or where a precipitate is to be dried and weighed without ignition, its use becomes more and more advisable. The student will find it convenient to provide himself with three or four porcelain Gooch crucibles and a platinum cap (made of thin foil) for ignition.

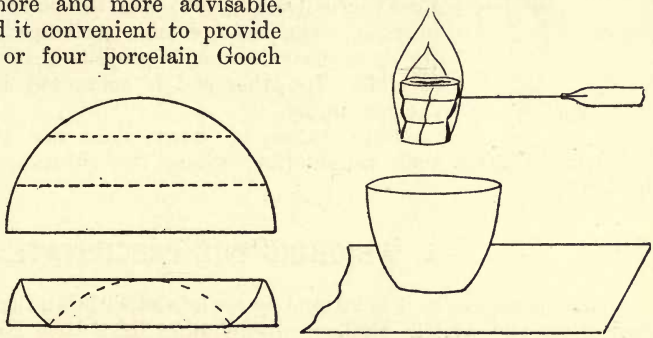


Fig. 57.

As the student frequently makes use of filter papers, he may now proceed to estimate the ash of the papers he intends using.

Take a porcelain or platinum crucible; place it in a triangle on a tripod, and gently heat up to a dull red. Keep it at this temperature for ten minutes. Remove the flame, and in two or three minutes transfer to the desiccator. When cool (in ten to fifteen minutes) quickly weigh the crucible, replace it in the desiccator and reweigh after five minutes. This is simply a check. If this weight is not the same as the previous one, the operation must be continued till two successive weighings do not differ by more than ·0003 gm.

Take ten of the papers, fold them and incinerate them one by one on the platinum wire, as before directed, allowing the ash to drop into the crucible. When the ash of the ten papers has been transferred to the crucible, place it on the tripod and ignite at a red heat for ten minutes, carefully stirring the ash to make sure that no black particles of unconsumed carbon remain. Remove the flame, and after two or three minutes place the crucible in the desiccator, and when cool weigh as before. Ignite for another five minutes, and repeat the desiccation and weighing. Then assuming

Weight crucible,	. .	18·2435 gms.
,, ,,	+ ash,	18·2527 ,, (first weighing)
,, ,,	,,	18·2525 ,, (second ,,)
∴ Weight of ash (difference)		·0090 ,,

∴ Weight of ash of one paper $= \frac{\cdot 0090}{10}$ gm. = ·0009 gm. And when one of

these papers is incinerated with a precipitate, this weight must be deducted from the joint weight to obtain the true weight of the precipitate.

It is of importance that when weighing the crucible alone the preliminary incineration should be carried out as directed. A few minutes' heating will not suffice, and half an hour or an hour will be too long. Again, if the precipitate is to be incinerated over the blast, the crucible in the preliminary ignition should be heated for about five minutes over the same blast. It is only by careful preliminary and after incineration, combined with systematic desiccation and weighing, that uniform results may be expected.

To save delay in weighing and gain by absorption of moisture from the air, place weights approximately lower than the probable weight of the crucible and precipitate on the pan. A little experience is here necessary, but the habit should be cultivated from the outset.

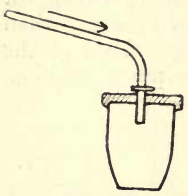


FIG. 58.

With some precipitates ignition in a current of oxygen, coal gas, hydrogen or carbon dioxide may be advisable. Rose's crucible (fig. 58) will be found serviceable for this purpose. The pipeclay tube is clamped on a retort or other stand, so that its nozzle projects through the lid into the crucible. Its other end is connected by rubber tubing to the gas supply.

Bulb tubes of hard glass are sometimes used for ignitions in gases such as chlorine, where the substance ignited is not to be weighed.

8. WEIGHING THE PRECIPITATE.

This operation, as it is intimately connected with ignition and the use of the desiccator, and as the methods of weighing have been described, will only be briefly noticed here.

When selecting a crucible for a given precipitate, besides considering the material of the crucible and the nature of the precipitate, some thought must be given to the weight and volume of the precipitate and the size and weight of the crucible. If the student has two porcelain crucibles weighing 15·+ and 6·+ gms. respectively, he will select the smaller crucible if it will conveniently hold the precipitate, as there is less liability to error through condensation of moisture. The less the surface exposed the less the condensation, and with a large crucible and very small precipitate the percentage error thus introduced may be serious.

The precipitate is sometimes weighed (without ignition) on counterpoised papers (or on a weighed filter paper); but as paper is hygroscopic, this method should be replaced by the Gooch crucible. When this is not available, the two papers are dried at 100° C. and counterpoised on the balance pans, roughly by clipping, and then by a rider. Both papers should then be subjected to the same treatment, one paper being run as a blank beside the other containing the precipitate. The papers, after the usual washing, are dried, transferred to the desiccator and weighed, making allowance for the rider previously used, the difference in weight giving the weight of the precipitate.

THE ATOMIC WEIGHTS OF THE CHEMICAL ELEMENTS.*

Name.	Symbol.	H=1.	H=1·008.	Name.	Symbol.	H=1.	H=1·008.
Aluminium	Al	26·9	27·1	Neodymium	Nd	142·5	143·6
Antimony	Sb	119·3	120·2	Neon	Ne	19·9	20
Argon	Ar	39·6	39·9	Nickel	Ni	58·3	58·70
Arsenic	As	74·4	75·0	Nitrogen	N	13·93	14·04
Barium	Ba	136·4	137·40	Osmium	Os	189·6	191·0
Bismuth	Bi	206·9	208·5	Oxygen	O	15·88	16·00
Boron	B	10·9	11·0	Palladium	Pd	105·7	106·5
Bromine	Br	79·36	79·96	Phosphorus	P	30·77	31·0
Cadmium	Cd	111·6	112·4	Platinum	Pt	193·3	194·8
Caesium	Cs	132	133	Potassium	K	38·86	39·15
Calcium	Ca	39·8	40·1	Praseodymium	Pr	139·4	140·5
Carbon	C	11·91	12·0	Radium	Rd	223·3	225
Cerium	Ce	139	140	Rhodium	Rh	102·2	103·0
Chlorine	Cl	35·18	35·45	Rubidium	Rb	84·8	85·4
Chromium	Cr	51·7	52·1	Ruthenium	Ru	100·9	101·7
Cobalt	Co	58·56	59·00	Samarium	Sm	148·9	150
Columbium	Cb	93·3	94	Scandium	Sc	43·8	44·1
Copper	Cu	63·1	63·6	Selenium	Se	78·6	79·2
Erbium	Er	164·8	166·0	Silicon	Si	28·2	28·4
Fluorine	F	18·9	19·0	Silver	Ag	107·12	107·93
Gadolinium	Gd	155	156	Sodium	Na	22·88	23·05
Gallium	Ga	69·5	70·0	Strontium	Sr	86·94	87·60
Germanium	Ge	71·9	72·5	Sulphur	S	31·83	32·06
Glucinum	Gl	9·03	9·1	Tantalum	Ta	181·6	183
Gold	Au	195·7	197·2	Tellurium	Te	126·6	127·6
Helium	He	4	4	Terbium	Tr	158·8	160
Hydrogen	H	1·000	1·008	Thulium	Tl	202·6	204·1
Indium	In	113·1	114·0	Thorium	Th	230·8	232·5
Iodine	I	125·90	126·85	Thulium	Tm	169·7	171
Iridium	Ir	191·5	193·0	Tin	Sn	118·1	119·0
Iron	Fe	55·5	55·9	Titanium	Ti	47·7	48·1
Krypton	Kr	81·2	81·8	Tungsten	W	182·6	184
Lanthanum	La	137·9	138·9	Uranium	U	236·7	238·5
Lead	Pb	205·35	206·9	Vanadium	V	50·8	51·2
Lithium	Li	6·98	7·03	Xenon	X	127	128
Magnesium	Mg	24·18	24·36	Ytterbium	Yb	171·7	173
Manganese	Mn	54·6	55·0	Yttrium	Y	88·3	89·0
Mercury	Hg	198·50	200·0	Zinc	Zn	64·9	65·4
Molybdenum	Mo	95·3	96·0	Zirconium	Zr	89·9	90·6

* From Report of the Committee on Atomic Weights,—F. W. Clarke, *J. Am. Soc.*, 1903, vol. xxv. No. 1.

Note on the Table of Atomic Weights.

The student will see that two values are placed opposite each element, one being based on the unit H = 1 and the other on the unit H = 1·008 or O = 16. In the course of his analytical work the student must take his values from one of these two columns, and from one only. Commencing on the assumption that H = 1, he will take all his values from the first column, but on the assumption that H = 1·008 (or O = 16), he will take them from the second column.

Some of the figures given in Parts II. and III. of this work do not agree with those in the table just given. When these sections were being written this table was not to hand, hence the discrepancies, for which the authors apologise, and ask the student to be good enough to refer to this table for all atomic weights, and substitute the figures in the table for those in the text. The student is advised to work from the second column.

9. CALCULATION OF RESULTS.

The conditions essential to accurate gravimetric analysis have been given. As a rule such estimations come under one of four classes—

(*a*) **Direct Estimations.**—These are the most usual and accurate methods of gravimetric analysis. The element sought is precipitated and weighed generally as a compound, definite in composition.

(*b*) **Direct Estimation by Loss.**—Here the element sought is volatile or forms a volatile compound and is driven off, the weight being taken as the volatilisation loss.

(*c*) **Indirect Estimations.**—When the previous methods are difficult these are used. If, for instance, **Na** or **K** are to be determined, unite them to **Cl** or SO_4, say to the latter, and weigh the joint sulphates. Call this weight *a*. Now estimate the SO_4 present. Call this weight *b*. From these two weights the **Na** and **K** present may be calculated. Let *x* gms. be the **Na** present and *y* gms. the **K** present, and let P be the weight of two atoms of **Na** ($P = Na_2 = 46$) and Q that of **K** ($Q = K_2 = 78$) and R the molecular weight of SO_4 ($R = 96$). Let *m* and *m'* gms. be the SO_4 united with **Na**+**K** respectively.

Given. $PR + QR = a$

$m + m' = b$

also that $\frac{x}{m} = \frac{P}{R}$ or $m = x\frac{R}{P}$

and $\frac{T}{m'} = \frac{Q}{R}$ or $m' = T\frac{R}{Q}$

Problem. Solve the two equations—

(1) $x + m + y + m' = a$

(2) $m + m' = b$

Replace *m* and *m'* in terms of *x* and *y* as given. Then by the usual algebraic methods we get the following values for *x* and *y*—

$$x = \frac{P}{R(Q-P)} \quad [b(Q+R) - aR]$$

$$y = \frac{Q}{R(Q-P)} \quad [aR - b(R+P)]$$

Replacing P, Q and R by the values given we obtain—

$$x = \cdot 09024(29b - 16a) = 2 \cdot 617b - 1 \cdot 444a$$

$$y = \cdot 05078(48a - 71b) = 2 \cdot 437a - 3 \cdot 605b$$

If many estimations of this nature are to be made, the chemist may save time in calculations by constructing to scale (a vertical height of 10″ or will give a suitable size) a diagram as shown in fig. 59. To obtain accurate results the figure must be carefully plotted.

One gram Na_2SO_4 contains ·317 gm. **Na** and ·683 gm. SO_4

„ „ K_2SO_4 „ ·448 „ **K** „ ·552 „ „

Plot these distances as shown on the vertical lines. Join the various points as shown.

Suppose analysis shows that one gram of the mixed sulphates gives ·624 gm. SO_4. Slide the rule along parallel to the vertical lines till the 6·24 mark on the rule meets the upper diagonal. The **K** and **Na** are read directly on the scale, and a simple calculation then gives the **K** and **Na** in the joint sulphates if their weight be not exactly one gram.

This illustration serves to show graphically the variations of such a mixture. If, however, in the methods of calculation given above logarithms are used, the saving of time vanishes, and the algebraic expressions have the further advantage of being applicable to all sorts of mixtures, whilst with the graphical method a fresh diagram must be prepared for chlorides of

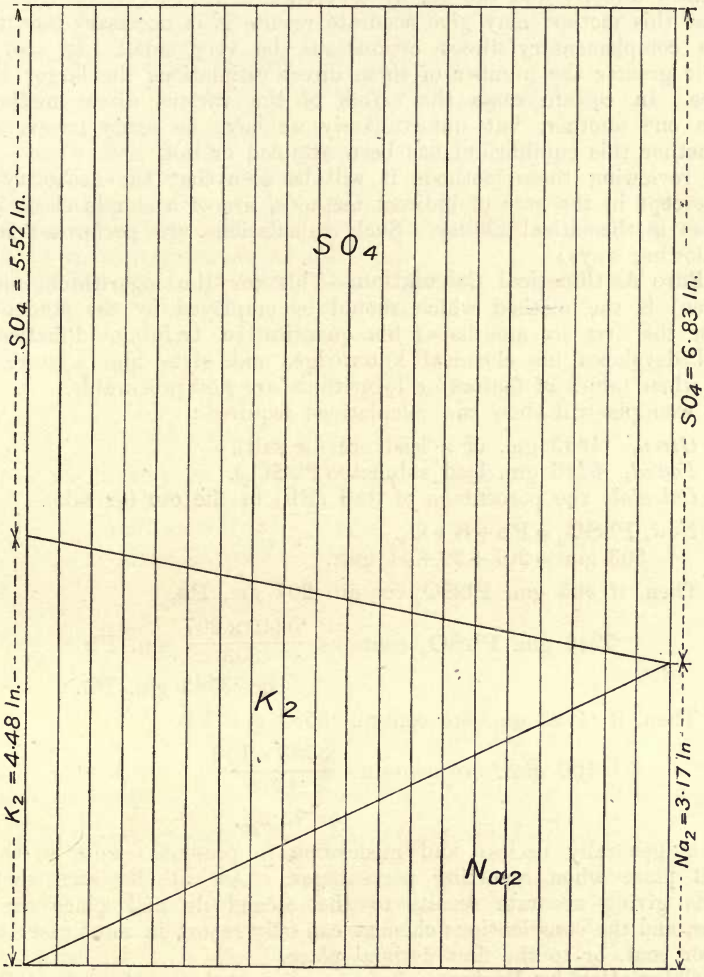


FIG. 59.

these two metals. It will be noticed that the delicacy of such methods increases as—

1. The atomic weights of the metals are low.
2. The difference between these weights increases.
3. The greater the atomic or molecular weight of the common acid.
4. The nearer the ratio $x : y$ approaches their atomic weights.

(*d*) **Estimations by Difference.**—In the present state of the science of chemistry certain elements such as oxygen and boron cannot be determined

accurately by direct methods. For instance, in the ultimate analysis of cane sugar the carbon and hydrogen are determined directly, and the oxygen is estimated by deducting the weight of the carbon plus the weight of the hydrogen from the weight of sugar taken for analysis. Again, Fe and Al are precipitated together and weighed as the oxide. The Fe is then determined directly and the Al by difference.

That this method may give accurate results it is necessary that the error in the complementary direct estimations be very small. It also is true that the greater the number of these direct estimations the larger the error will be. In certain cases the errors of the various direct methods may balance one another, but unfortunately we have no ready means of knowing whether this equilibrium has been attained or not.

On reviewing these methods it will be seen that the necessary calculations, except in the case of indirect methods, are of a simple class, involving no great mathematical ability. Such calculations are performed in one of the following ways:

1. **Pure Arithmetical Calculation.**—This (or the logarithmic method to be given) is the method which should be employed by the student during at least the first six months of his quantitative training. Practice in this method developes his chemical knowledge, and gives him a store of data useful when tables of factors or logarithms are not procurable.

An example will show the calculations required:

Given, ·4893 gm. of a lead ore (or salt).
Found, ·5246 gm. lead sulphate ($PbSO_4$).
Calculate the percentage of lead (Pb) in the ore (or salt).

Now, $PbSO_4 = Pb + S + O_4$.
303 gm. $= 207 + 32 + 64$ gms.

Then, if 303 gm. $PbSO_4$ contain 207 gm. Pb,

·5246 gm. $PbSO_4$ contains $\frac{\cdot 5246 \times 207}{303}$ gm. Pb

or ·3583 gm. Pb.

Then, if ·4893 gm. ore contain ·3583 gm. Pb,

100 gms. ore contains $\frac{\cdot 3583 \times 100}{\cdot 4893}$

or 73·2%.

It is generally useless and misleading to present results in the second decimal place when reporting percentages. As will be seen shortly, the methods giving accurate results to the second decimal place are few in number, and the conscientious chemist can only report in most cases to tenths of a per cent. or to the first decimal place.

2. **Calculation by Factors.**—In many text-books on Analytical Chemistry tables of factors are given, with the object of lessening the labours of the chemist. These factors should not be used by the student until he is certain that he can obtain the same results by the previous method, and that he understands how such factors are obtained.

Taking again the example concerning a lead ore, the student will find in a Table of Factors, in the column "Found" (or "Weighing Form"), opposite "Lead," $PbSO_4$, and in the column "Sought," Pb, and in the column "Factor," ·6831. Briefly, he has a precipitate of $PbSO_4$, and he wishes to ascertain the weight of lead in this precipitate. He does this by multiplying the weight of the precipitate by the factor ·6831.

Weight of Lead = ·5246 × ·6831 = ·3583 gm.

The remainder of the calculation is worked as before.

The factor ·6831 is derived thus:—

303 gms. $PbSO_4$ contain 207 gms. Pb.

1 „ „ " $\frac{207}{303}$ „ „ = ·6831 gm. Pb.

Then if 1 gm. $PbSO_4$ contain ·6831 gm. Pb,

·5246 „ „ $\frac{·5246 \times ·6831}{1}$ gm. Pb.

That is, the weight of the precipitate multiplied by the factor gives the weight of the lead in the precipitate.

Tables of factors are compiled on this basis, giving factors for all the more common elements and precipitates. These tables will be found in the more advanced works, supplementary to this book.

3. Calculation by Logarithms.—The student conversant with the use of logarithms will save much time by applying them to these calculations.

In the example given, the calculation required is

$$\text{Wt. } PbSO_4 \times \frac{207}{303} \text{ (or factor)} \times \frac{100}{\text{weight of ore}} = \% \text{ Pb},$$

$$\text{or} \qquad ·5246 \times ·6831 \times \frac{100}{·4893} = \% \text{ Pb},$$

$$\text{or} \quad \log ·5246 + \log ·6831 + \log 100 - \log ·4893 = \text{Log } \% \text{ Pb}.$$

log ·5246 = $\bar{1}$·719828.
„ ·6831 = $\bar{1}$·834484
„ 100 = 2·000000.

1·554312
„ ·4893 $\bar{1}$·689575

„ 1·864737 = Log % Pb.
Percentage Pb = 73·24.

As in some one or more of the many operations necessary, error may occur, it is evident that these results do not represent the true quantities of the various constituents, but differ from them by some slight fraction. With a good method this fraction or error should be less than $\frac{1}{500}$. As a general rule it may be taken that results are only accurate to the first decimal place, though with extreme care results have been obtained accurate to the third place. Such careful work, however, demands too much of the chemist's time, and is unsuited for commercial work. When analysing mixtures such as rocks, ores, alloys, etc., or chemical compounds, where a number of determinations are required, certain checks of more or less value may be applied to the results.

(*a*) **Check on Results of the Analysis of a Mixture.**—Take, for example, a complex sulphide ore containing Cu Fe Pb Zn and S. Five determinations are here necessary, and the sum of the weights found of these elements should equal the weight of the ore taken for analysis. If this is not so, error has crept in; and even if these weights correspond, there is still the possibility of error; one element may be over-estimated and another under-estimated, and the total be correct. The probability of this is not great. but the student must remember that the possibility still exists.

It must also be remembered that the larger the number of elements to be estimated, the greater the difficulty in getting the total percentages to equal 100. When four elements have to be estimated, the student's total percentage should lie between 99·5% and 101%, and when seven or eight separate estimations must be made it should lie between 98·5% and 102%. These figures are not intended to absolutely define the limits of good work; the nearer the total is to 100 the better. In all cases the student must make duplicate determinations of every element. As a rule, these should agree within one-tenth of a per cent., *eg.* two results are 14·36% and 14·44%. When these do not agree, the student frequently makes the mistake of performing *two* more estimations. If the work has been done with reasonable care, the probability is that one of the two is correct, or nearly so. Make *one* more estimation. Then, if this agrees with one of the two, the safe assumption is that that one is correct; but if the three estimations all differ, either the method or the work must be condemned, and the student may take it that *his* work is at fault. Let him re-read the instructions, see that his weighings are correct, and that he follows every instruction to its minutest detail, and then proceed afresh with the analysis. His perseverance will generally meet its due reward. Confidence can be obtained in no other way.

(*b*) **Checks on the Analysis of Chemical Compounds.**—As a chemical compound consists of elements bound together in *definite* proportions, it follows that if such compounds are approximately pure, then from our knowledge of these proportions a check can be obtained.

A sample of ferrous sulphate is purified and analysed for iron. The molecular weight of $FeSO_4,7H_2O$ is 277·7, and the molecule contains 55·88 parts by weight of Fe, and 31·98 parts of S. The percentage of Fe in the molecule is $\frac{55{\cdot}88 \times 100}{277{\cdot}7}$. The percentage of Fe found by analysis should correspond with this. A similar check can be applied to the sulphur present.

This method of checking may be applied to isomorphous mixtures of bases and acids, *e.g.* $CaSO_4$ and $PbSO_4$. Suppose such a mixture has been analysed, and the following percentages of bases and acids found:—

$$CaO = 19{\cdot}48\%,\ PbO = 38{\cdot}78\%,\ SO_3 = 41{\cdot}74\%.$$

Convert these into equivalents by dividing by their molecular weights—

$CaO = \frac{19{\cdot}48}{56} = {\cdot}348$	$SO_3 = \frac{41{\cdot}74}{80} = {\cdot}522$
$PbO = \frac{38{\cdot}78}{223} = {\cdot}174$	
Total for bases = ·522	Total for acids = ·522

When the equivalents for bases agree with those for acids, the student may safely assume that the work is correct. Unfortunately this method of checking cannot be carried very far, as we are frequently uncertain as to the form of combination in which an element or group of elements exists.

The student commencing the study of quantitative methods should perform his first estimations either on salts known to be practically free from impurities, or on substances which have been analysed by the demonstrator. The latter plan is preferable; the student performs the analysis in duplicate or till concordant results are obtained, and then brings his results to the demonstrator, who rejects or accepts them according as they are right or wrong.

CHAPTER III.

MISCELLANEOUS OPERATIONS AND REMARKS.

In Chapter I. the main operations incidental to the typical gravimetric estimation have been considered. In this chapter certain matters, some of which properly belong to the sphere of Practical Physics, will be dealt with.

(1) THE PURIFICATION OF SALTS AND REAGENTS.

In quantitative analysis certain substances, generally liquids, are added to the material examined, for the purposes of solution and precipitation. It is evident, then, that these added substances either must not contain the element sought, or if they do, this quantity of the element must be accurately determined and allowed for. This may be done either by analysing each of the reagents used, or by running what is called a 'blank' estimation. In the blank all the conditions of treatment and reagents used should be the same as in the actual analysis, except that the substance being examined is not present. Thus, if any of the element sought is present in the reagents used, the amount present is ascertained, and is deducted from the amount found in the actual analysis.

If the student is fortunate enough to be provided with reagents 'guaranteed' pure (such as "Merck's"), there will be little need to perform 'blank' estimations; but as the metallurgical chemist is frequently in localities where it may be difficult to procure pure chemicals, he must understand some of the methods employed for purification. The likely impurities in the various reagents have been touched on in the section on Qualitative Analysis.

In the last paragraph of Chapter I. the student was instructed to commence his quantitative work either on pure salts or on materials checked by the demonstrator. If, then, he is to check his work by using pure salts, it is advisable, even if the salt is supposed to be pure, to subject it to purification.

This may be carried out by many methods or combinations of methods, of which the following are the most common:—

(*a*) Purification by Repeated Crystallisation.
(*b*) „ „ Precipitation by Double Decomposition.
(*c*) „ „ „ „ Change of Solvent.
(*d*) „ Sublimation.
(*e*) „ „ Distillation.

(*a*) **Purification by Crystallisation.**—If the salt to be purified and the impurities contained are soluble in water, the salt may be separated from the impurities by crystallisation, provided—

1. That there is a considerable difference between the solubility of the salt and that of the impurities.

2. That the salt does not combine with any one of the impurities to form a double salt.

3. That if a double salt is to be separated, this double salt must be stable, that is, not easily separated into its constituent simple salts.

In ascertaining whether these conditions are satisfied or not, the student must bring to bear an accurate and detailed knowledge of theoretical chemistry. When in doubt let him carefully analyse qualitatively the commercial salt, and then his (supposed) purified preparation.

The following are examples of salts that may be purified by crystallisation,—KCl, $BaCl_2$, $CuSO_4,5H_2O$, $ZnSO_47H_2O$, $K_2Cr_2O_7$, K_2SO_4, $Al_2(SO_4)_3,24H_2O$. Let the student select a 'commercial' brand of one of these salts, say, $CuSO_4,5H_4O$. Select a 500 c.c. beaker, and into it pour about 250 c.cs. water, and heat to boiling on a tripod and wire gauze. Add the roughly powdered salt, a little at a time, until an almost saturated solution is obtained. If the solution now appears dirty, it must be filtered through a *hot* funnel. A piece of lead pipe is wound round a glass funnel as in fig. 60, and is connected to a flask and delivery tube generating steam, which passing through the lead coil, heats the funnel. Coarse filter paper (grey) may be used for this filtration. The funnel must be kept hot throughout the filtration, or the salt will crystallise out on the paper. The filtrate in the beaker is now cooled quickly by immersing the beaker in a basin of cold water, or by running down its outer side a stream of cold water from the tap. A deposit of *small* crystals is thus obtained (slow cooling would produce large crystals). When cold, decant most of the liquid, and transfer the crystals to a pad of filter paper (grey), and when most of the remaining liquid has been absorbed, transfer the crystals to a clean beaker, and by the aid of heat dissolve them in the smallest possible quantity of water. Remove the beaker and contents and cool as before, and drain again on a filter pad until apparently dry; then carefully and firmly press thin layers of the crystals between clean filter paper, and transfer the crystals to a clean glass stoppered bottle.

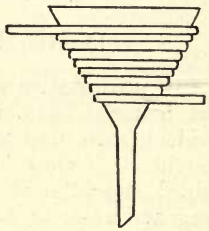


FIG. 60.

(*b*) **Purification by Precipitation by Double Decomposition.**—Purification by double decomposition is a repetition on the large scale of some one of the usual quantitative methods.

Suppose it is wished to prepare pure $CaCO_3$. The commercial carbonate is dissolved in HCl (in excess). NH_4HO and NH_4Cl are then added as in the usual gravimetric separation, any iron, etc. filtered off, and then $(NH_4)_2C_2O_4$ to precipitate CaC_2O_4. This precipitate is filtered, washed, redissolved, and again precipitated, to get rid of any traces of Mg that still remain. The precipitate is then repeatedly washed with hot water until all traces of soluble salts are removed. The precipitate is then redissolved and precipitated with $(NH_4)_2CO_3$, thoroughly washed and dried. Any compounds present in the commercial $CaCO_3$ that will give a precipitate with $(NH_4)_2CO_3$ must be removed before precipitation by this reagent. Care must also be taken that the precipitating reagent contains no impurity that can affect the result.

(*c*) **Purification by Precipitation through Change of Solvent.**—This depends on the fact that the solubility of a salt varies in different liquids, so that by adding to a water solution of the salt another liquid such as an acid or alcohol the salt is thrown down. In this way $BaCl_2$ or NaCl may be thrown down from a strong aqueous solution by passing through it HCl gas; or $FeSO_4$

by the addition of alcohol. This method may be combined with that by crystallisation.

The student may prepare pure $FeSO_4 7H_2O$ as follows :—Dissolve 50 gms. commercial $FeSO_4 7H_2O$ in water, *gently* heating till dissolved. Filter if necessary. To the warm filtrate add a few drops of H_2SO_4, and then about an equal volume of methylated or rectified spirit. Stir, and the $FeSO_4 7H_2O$ is precipitated as a bluish white granular powder. Filter and wash with spirit, dry and preserve in a glass stoppered bottle.

(*d*) **Purification by Sublimation.**—This method is not of such wide application as the preceding. As an example, the student may take once-sublimed iodine and purify it as follows :—Place about 1 ounce or 30 gms. iodine, mixed with 2 gms. KI (to remove any Cl), in a 150 c.c. glass retort with a short tube, and connect the tube with an adaptor, or run it into a 250 c.c. glass flask. Apply gentle heat with a bunsen burner under the retort, and violet vapours come over and condense in the adaptor or flask. Continue the operation till the greater part of the iodine has passed over.

The iodine may be removed from the adaptor or flask by gently warming the outside, when it becomes detached in masses and is removed and transferred to a wide-mouthed glass stoppered bottle.

(*e*) **Purification by Distillation.**—This method is more frequently used after preliminary chemical treatment than alone. Absolute alcohol may be prepared from rectified spirit by treatment with quicklime or anhydrous calcium chloride, either of which on prolonged contact for twelve to twenty-four hours absorbs the water from the alcohol, forming hydroxide or hydrated chloride of lime, from which the alcohol is then separated by distillation.

Again, HNO_3 may be purified from chlorine as follows :—Dilute 500 c.cs. crude HNO_3 (S.G. 1·38) with 200 c.cs. water. Add $AgNO_3$ solution till a precipitate ceases to form. Then add a slight excess of $AgNO_3$. Let the precipitate settle, and decant the acid into a large glass retort (1 litre). Add one or two grams of KNO_3 free from chlorine. Distil, and test a few drops of the distillate diluted with distilled water for chlorine, and reject any portions containing this element.

The limits of this work forbid any further treatment of this subject. The methods briefly described are varied, and will serve as a basis from which the thinking student may proceed to work in any particular case; and to meet with success the student must bring to bear considerable ingenuity, coupled with a sound knowledge of theoretical chemistry. When commencing a gravimetric analysis, the student must always consider the possibility of the reagents used containing impurities affecting the results of the analysis. In routine work it is advisable that the chemist procure guaranteed reagents.

(2) THE QUANTITATIVE NOTE-BOOK.

By this is meant, not a small pocket-book, but a respectable margined book, about 22 cm. × 18 cm. × 2 cm. In this book must be made all the *original* entries, such as figures of weighings, calculations, and results. Briefly, the book must contain a full systematic account of every analysis undertaken. It is perhaps going too far to lay down hard and fast rules regarding the details of note-book entries, yet the student must from the outset keep his notes neatly and in a form intelligible at a glance to the chemist, and to attain this end he should at the outset devote at least a few hours to the drawing out of a suitable scheme. As he is inexperienced as yet in quantitative work, an example of a few pages from a note-book is given for his guidance.

Calculations.

Det. 1. *Given*—·5122 gm. subst. Found, ·1630 gm. **CuO**.
Required—Percentage of **Cu**.

·1630 gm. **CuO** give $\frac{·1630 \times 63}{79} = ·1299$ gm. **Cu**.

```
·1630
  63
 4890
9780
79)10·2690(·1299
  79
 236
 158
  789
  711
   780
```

One molecule **CuO** contains 63 parts **Cu** and 16 parts **O** by weight

Percentage **Cu** $= \frac{·1299 \times 100}{·5122} = 25·36\%$

```
·5122)12·990(25·36
      10244
       27460
       25610
        18500
        15366
         31340
```

Det. 2. *Given*—·5122 gm. subst. Found, ·4732 gm. $BaSO_4$.
Required—Percentage SO_4.

·4732 gm. $BaSO_4$ contain $\frac{·4732 \times 96}{233} = ·1949$ gm. SO_4.

```
·4732
  96
28392
42588
233)45·4272(·1949
  233
 2212
 2097
  1157
   932
  2252
```

One mol. $BaSO_4$ contains 137 parts **Ba** and 96 parts SO_4 by weight.

Percentage $SO_4 = \frac{·1949 \times 100}{·5122} = 38·05\%$.

```
·5122)19·490(38·05
      15366
       41240
       40976
        2640
```

Det. 3. *Given*—·4880 gm. subst. give ·1741 gm. H_2O.
Required—The percentage of H_2O.

$$\text{Percentage } H_2O = \frac{\cdot 1741 \times 100}{\cdot 4880} = 35{\cdot}68\%$$

$$\begin{array}{r} \cdot 4880)17{\cdot}410(35{\cdot}68 \\ 14640 \\ \hline 27700 \\ 24400 \\ \hline 33000 \\ 29280 \\ \hline 37200 \end{array}$$

Check. Calculate the theoretical percentage of **Cu**, SO_4 and H_2O in $CuSO_4$, $5H_2O$. Substituting atomic wts. $63{\cdot}2 + 32 + 64 + 90 = 249{\cdot}2$.

$$\text{Percentage } Cu = \frac{63{\cdot}2 \times 100}{249{\cdot}2} = 25{\cdot}4$$

$$\begin{array}{r} 249{\cdot}2)6320{\cdot}0(25{\cdot}4 \\ 4984 \\ \hline 13360 \\ 12460 \\ \hline 9000 \end{array}$$

$$\text{Percentage } SO_4 = \frac{96 \times 100}{249{\cdot}2} = 38{\cdot}5$$

$$\begin{array}{r} 249{\cdot}2)9600{\cdot}0(38{\cdot}5 \\ 7476 \\ \hline 21240 \\ 19936 \\ \hline 13040 \end{array}$$

$$\text{Percentage } H_2O = \frac{90 \times 100}{249{\cdot}2} = 36{\cdot}1$$

$$\begin{array}{r} 249{\cdot}2)9000{\cdot}0(36{\cdot}1 \\ 7476 \\ \hline 15240 \\ 14952 \\ \hline 2880 \end{array}$$

Note.—On comparing the check figures with those obtained from actual analysis, the student will conclude that as his **Cu** percentage is nearly correct, the somewhat large error on the SO_4 and H_2O is due to faulty work, and not to the presence of impurities which have not been estimated, and which should have been detected in the qualitative examination. The results of the duplicates will probably confirm this conclusion.

Throughout these notes contractions may be used. Qual. An. = Qualitative Analysis ; Wt. = Weight ; Det. = Determination ; Diff. = Difference, and so on.

Whenever the composition of a substance is unknown (and this is frequently the case), the quantitative analysis must be preceded by a qualitative examination. This important preliminary step must never, in such cases, be omitted.

As the student is generally working from either written or printed instructions, it is unnecessary to enter a full description of the analysis. An indication of the methods used and reference to source of instructions will suffice.

The left-hand page is reserved for calculations, which should be neatly worked out either arithmetically or by logarithms. In the earlier stages of his work factors should not be used unless constructed by the student. On this page come also any check calculations.

On the right-hand page are entered all weighings. These must be entered directly the weights are removed from the balance, the note-book being within convenient reach. Memory can never be trusted in such matters. A space of two lines may be left between each determination, and of one line between successive steps in any one determination. The entries may be made in ink or pencil, preferably in ink, and a few spare minutes devoted to underlining headings with red ink adds to the appearance and readability of the notes.

Note.—In the Gooch method the figures for ash do not appear.

Substance No. 4.

Qual. An. Found.	1. Cu. 2. SO_4. 3. H_2O.		
Quant. An.			
1 Det. of Cu.	Grav. ppn. by KHO	(details p.)	
	Tube + Subst.	= 5·3211	
	,, less ,,	= 4·8089	
	Subst. taken	= 0·5122	
	Wt. Cr.	= 6·4207	
	,, ,, + pp. + ash	= 6·5859	(20 min. inc.)
	,, ,, ,, ,,	= 6·5847	(30 ,, ,,)
	,, ,, ,, ,,	= 6·5842	(40 ,, ,,)
	Diff., pp. + ash	= 0·1635	
	Less ash (·0005)	= 0·1630	
2 Det. of SO_4	Grav. ppn. by $BaCl_2$	(details p.)	in filtrate
	Wt. Cr.	= 5·8621	
	,, ,, + pp. + ash	= 6·3378	(min. inc.)
	,, ,, ,, ,,	= 6·3364	(,, ,,)
	,, ,, ,, ,,	= 6·3358	(,, ,,)
	Diff., pp. + ash	= 0·4737	
	Less ash (·0005)	= 0·4732	
3 Det. of H_2O	Grav. loss by heating in an open crucible gives the H_2O.		
	Tube + Subst.	= 4·8089	
	,, less ,,	= 4·3209	
	Subst. taken	= 0·4880	

Substance No. 4—*continued.*

	Wt. Cr.	= 6·4201	
	,, ,, + Subst.	= 6·9081	
	,, ,, ,, ,,	= 6·7368	(min. heating)
	,, ,, ,, ,,	= 6·7345	(,, ,,)
	,, ,, ,, ,,	= 6·7341	(,, ,,)
	Wt. Water lost	= 0·1741	

Results.

Found.		Theoretical Calculated.	
Cu	25·36%	Cu	25·4%
SO_4	38·05%	SO_4	38·5%
H_2O	35·68%	H_2O	36·1%
Total	99·09%	Total	100·0%

(3) CERTAIN PHYSICAL DETERMINATIONS.

It is generally expected of the chemist that, if required, he is able to make certain physical determinations which are of value in analytical processes. Of these, the most important are determinations of Specific Gravity, Melting and Boiling Points, and Vapour Density. It is not intended here to do more than briefly touch on these matters. For further information the student is referred to text-books on Practical Physics, Ostwald's Physico-chemical Measurements, or the larger works on Analytical Chemistry.

Specific Gravity.—The following tabulation gives some of the most important methods used in the determination of the Specific Gravity of Solids and Liquids :—

Solids.—1. *Not acted on by water.*—A lump is weighed in air and then in water, and the S.G. calculated from the weighings.

2. *Acted on by water.*—A lump is weighed in air and then in some liquid such as naphtha, benzene, or alcohol of known S.G., and the S.G. calculated as before.

3. *In a powdered state.*—A small S.G. bottle (Pyknometer) is weighed full of water. Then a weighed quantity of the powder is introduced, and from the quantity of water displaced and the weight of powder taken the S.G. is calculated.

Liquids.—1. *Approximately* by the Hydrometer.

2. *Accurate to ·001* by a 1 c.c. pipette.

3. *Accurate to ± ·00002* by the Sprengel Tube.

In all of these methods the temperature is important; and where glass vessels are weighed, care must be taken that a uniform method of wiping is adopted, or a *varying* film of moisture will exist on the surface. Before weighing, the glass should be carefully dried with a clean, soft, linen cloth, and this treatment should be followed in all cases.

As in his mineralogical and physical laboratory work the student has already had practice in determining the S.G. of solids, these will not be considered here.

The Specific Gravity of liquids may generally be determined by the Hydrometer, the S.G. being read directly from the scale on the stem, either in terms of water as a standard of 1·000 (or 1000), or in degrees Baumé. The following formulæ serve to convert degrees Baumé to the usual standard :—

$$\text{For liquids heavier than water, S.G.} = \frac{144}{144 - n}$$

$$\text{,, ,, lighter ,, ,, S.G.} = \frac{145}{135 + n}$$

where n = the number of degrees Baumé.

Thus 24° B. for a liquid lighter than water corresponds to—

$\frac{145}{135+24} = \frac{145}{159} = \cdot 912$. These results are only approximate, and for accurate conversions the student may consult the tables given in more advanced works.

Rapid and accurate determinations may be made by the method described by Ostwald. A 1 c.c. pipette with almost capillary tubes is marked to hold 1 c.c. of water. Its weight when empty and dry is carefully ascertained. It is then filled (at the same temperature as before) to the mark with the liquid and the point carefully dried. It is then reweighed, and the weight gives the S.G. directly. For convenience in weighing, the pipette is laid flat on a small wire stand, the weight of which is accurately determined.

For more accurate determinations the student may consult the works referred to.

Determinations of Melting and Boiling Points and Vapour Density belong more to the sphere of General than Metallurgical Chemistry, and are simply mentioned to call the student's attention to certain auxiliary Physical methods which may in some cases be of service when determining the constitution of a liquid or solid.

(4) POINTS ON LABORATORY WORK.

(*a*) **Economy of Time.**—Economy of time is best secured by working from first to last as carefully as possible. "The more haste the less speed" holds here as in other things. "Quality" must be attained before attempting "Quantity." This must not be construed, as is sometimes done, into wasting time. A slow filtration goes no faster by staring at it, and in the time so lost a crucible could be ignited and weighed, or some other operation commenced. As many operations should proceed concurrently as can be attended to without confusion. At the outset one or two operations may demand the student's whole attention, but as time goes on his capacity for work will increase; and if, preparatory to his day's practical work, he carefully read up his instructions and map out his scheme of work, further time will be saved. He should so arrange his work that at no time is he idle, and at no time is he 'rushed.' If in doubt, it is preferable to err on the side of wasting time than to 'rush' a number of operations, as the repetition of work likely to ensue from undue haste will in the end consume much more time than would be required to do the work thoroughly in the first place. The student, then, in this matter must exercise to the full his common-sense, and carefully consider how far he may run several operations concurrently without affecting the thoroughness of either.

He will also find that time is saved by *strictly* following all instructions laid down. If inclined to criticise any instruction as unnecessary or as an undue refinement, he must remember that it is inserted for some *definite* purpose, which may be revealed to him on more mature consideration. There

is no 'short-cut' to the end desired except that of patient and intelligent work.

(*b*) **Bench Work.**—As the experienced employer can at a glance estimate a skilled workman's value by the clean, free style in which he handles his tools, so the experienced chemist will at a glance discern from his work-bench the skill and value of the student. While not denying that accurate and quick results may be obtained on a bench littered with apparatus, clean and unclean, and in an order known (if to anyone) only to the student, such a student must remember that he is heavily handicapped if he seeks a living in the Chemical world, and at the very outset has earned a reputation for carelessness. All apparatus should be cleansed **immediately** after use, and unless required at once should be replaced in the locker on a clean sheet of white paper.

All apparatus on the bench should be set in order. Beakers, flasks, wash bottle, and funnels should not be indiscriminately mixed, but each beaker should be placed beside its respective filter funnel, and all other apparatus except the wash bottle placed in a row behind the filtration. Similar methods should be followed with other operations. Care should be taken to exclude all foreign matter from an analysis. Cigarette ash cannot add to the accuracy of an analysis. The same remark applies to reagent bottles covered with dust. Again, when conducting more than one operation at a time, or putting away an unfinished analysis, the various vessels should be labelled with neat paper labels, or better, with a special blue pencil. These remarks could be greatly multiplied, but perhaps the best advice that can be given to the student is that he look round him and criticise the work of any careless fellow-students. He may then notice that in some points he himself is not quite perfect; and to avoid giving openings to would-be critics, he must immediately set to work to remedy these deficiencies.

(*c*) **The Equivalent System of Reagents.**—This has been noticed previously, but a few additional remarks are necessary here. The student should form the habit of calculating the quantity of reagent required in every case. Thus 1 gm. **Zn** requires 30·8 c.cs. E. acid for solution. The equivalent of **Zn** is $\frac{65}{2} = 32{\cdot}5$, and 1 c.c. E. acid will dissolve 32·5 mgms. **Zn**, therefore 1 gm. **Zn** requires $\frac{1{\cdot}0000}{{\cdot}0325} = 30{\cdot}8$ c.cs. E. acid.

Again, 1 gm. **Cu** requires 31·5 c.cs. E. **KHO** for precipitation from solution as $Cu(OH)_2$. The equivalent of **Cu** is $\frac{63{\cdot}5}{2} = 31{\cdot}75$, and 1 c.c. E. **KHO** precipitates from solution 31·75 mgms. **Cu**. Therefore 1 gm. **Cu** requires $\frac{1{\cdot}000}{{\cdot}03175} = 31{\cdot}5$ c.cs. E. **KHO**. Again, on neutralising say 5 c.cs. 36 E. H_2SO_4 with E. **KHO** there are produced $5 \times 36 = 180$ equivalents of Na_2SO_4; and as the equivalent of Na_2SO_4 is $\frac{142}{2} = 71$ we have $180 \times 71 =$ 12780 mgms. or 12·780 gms. Na_2SO_4 in solution.

These calculations might be indefinitely extended, but the few given will be sufficient to show the simplicity of the equivalent system, and its suitability to the needs of the chemist who desires to conduct all operations under known and accurately defined conditions.

CHAPTER IV.

SIMPLE GRAVIMETRIC DETERMINATIONS.

In this chapter certain simple gravimetrie determinations will be considered in detail. In each case the following order is adopted :—

Apparatus and Chemicals required.
Method employed and reactions.
Details of the Analysis.
Calculation and Accuracy of Results.

Where no further apparatus than that already described is used, no details under this head will be given unless some special arrangement is adopted.

It is always assumed that before commencing an analysis the student has all apparatus thoroughly clean and in readiness.

Regarding the methods employed, brief notes will be given explaining the reactions on which the method is based, and any comments thereon which may aid the student. For reference on such points the student may consult *Quantitative Analysis* by Fresenius, or *Qualitative Analysis* by Prescott and Johnson. The student who wishes to excel must take advantage of these reference works, and should understand the reason for every step in the analysis. A merely mechanical attention to the instructions, however perfect, although it may yield good results, can never produce more than a 'rule-of-thumb' analyst.

In the detailed instructions for each analysis the student is to understand that he is never to weigh *exactly* quantities such as ·5 gm. or 1 gm. unless specially instructed to do so.

When performing filtrations he may use the Gooch or the ordinary method, unless specially instructed otherwise. The Gooch method is generally preferable; but as the paper method is more difficult and is still largely used, it is described in the instructions.

When instructed to incinerate a precipitate in a crucible, one of platinum may be used with advantage, provided it is not attacked by the material. If a platinum crucible is not available, porcelain may be used, and with care gives good results.

Calculations of results are not worked out in detail, an outline merely of the necessary steps being given. The student who has studied the foregoing pages will have little difficulty in completing the required calculations.

The authors would have much liked in every case to definitely state the degree of accuracy attainable by good work, but regret that, owing to the absence of data, they can do little more than state in many cases whether a method is regarded as good or otherwise. In simple estimations there is, as a rule, little difficulty in obtaining accurate results; but in complex substances, where an element has to be separated by precipitation from a number of

others, complete precipitation can rarely be obtained in one step, as traces of other elements are also precipitated. Such a precipitate must be redissolved and reprecipitated until the desired end is attained. In these cases the precipitate must be examined qualitatively to detect the presence of impurities. Too little stress is laid by many text-books on the necessity of re-solution and precipitation when dealing with complex substances. The student will find a good concrete example of the necessity of this procedure when he comes to the analysis of an insoluble silicate; and if he compare the older methods with those laid down in the paper of Dr Hillebrand, he will find that considerable discrepancies are accounted for by incomplete precipitation.

THE ESTIMATION OF COPPER IN COPPER SULPHATE, $CuSO_4,5H_2O$.

Apparatus, Chemicals, etc.—The usual equipment. The student may take for analysis the salt which he has previously purified, or he may be given a certain volume of solution prepared and checked by the demonstrator, in which case the preliminary solution being already effected, the analysis is to be proceeded with from that point.

Method, Reactions, etc.—The method here given is selected with the object of giving the student practice in the various manipulations of gravimetric analysis. Being rather tedious, it is not used by the chemist in routine work, and is replaced by the Cyanide, Iodide, or Electrolytic methods, which are given further on.

In the method here employed the copper is precipitated from solution as the hydroxide $Cu(OH)_2$ by means of a solution of KHO,

$$CuSO_4 + 2KHO = \underline{Cu(OH)_2} + K_2SO_4$$

and on boiling,

$$3Cu(OH)_2 = \underline{Cu(OH)_2,2CuO} + 2H_2O$$

a black hydrate of copper being formed. On gently heating the dried precipitate,

$$Cu(OH)_2 = CuO + H_2O$$

Fusion of the precipitate must be avoided or

$$5CuO = CuO,2Cu_2O + O_2$$

which will introduce an error of between 8% and 9% in the cupric oxide.

On incineration of the paper with traces of precipitate,

$$2CuO + C = 2Cu + CO_2$$

The ash is then treated with a few drops of HNO_3

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$$

And on evaporation and re-ignition

$$Cu(NO_3)_2,3H_2O = CuO + 2HNO_3 + 2H_2O$$

Cupric oxide being again formed, and from the total cupric oxide obtained the copper is calculated.

Details of the Analysis.—Transfer a few grams of the purified salt to a weighing tube. Insert the stopper and wipe the tube with a soft linen cloth. Weigh the tube and contents. Remove it from the balance and shake about

1 gm. into a 200 c.c. beaker. Reweigh the tube to obtain the exact weight taken.

To the salt in the beaker add 100 c.cs. distilled water. Apply heat till the salt is dissolved, and finally heat to boiling.

Now gradually add, a little at a time, an E. solution of **KHO**. About 9 c.cs. will be required. When precipitation is complete the solution should, on allowing the precipitate to settle, just appear colourless, and a drop removed on a glass rod should give an alkaline reaction with litmus paper.

The contents of the beaker are now boiled for two or three minutes, when the flame is removed and the precipitate allowed to settle.

Fit a paper in a filter funnel on a stand, and set a beaker underneath to catch the filtrate. Decant the solution down a glass rod on to the filter paper. Add 50 c.cs. boiling water to the precipitate. Let settle and again decant, and repeat the washing by decantation once more, and transfer, with the aid of the wash bottle jet, the precipitate on to the filter. Any precipitate adhering to the sides must be removed with a rubber-tipped glass rod. Now proceed to wash the precipitate and the paper by a number of small washes until no reaction is obtained on testing the washings with $BaCl_2$ for SO_4.

Cover the funnel lightly with a filter paper and place it in the water oven or air oven at 100° C. to dry. When the paper and precipitate appear dry remove the funnel and contents and carefully place them on a sheet of glazed paper. Remove as much as possible of the precipitate to a small weighed crucible (previously heated). Fold the paper, precipitate-side in, for incineration. Deposit the ash in the crucible, and from a glass tube or pipette deliver one drop of strong HNO_3 on the ash.

Gently warm the crucible for a few minutes to expel the excess of HNO_3, and then raise the temperature to dull redness, and maintain this temperature for ten minutes.

Remove the crucible to the desiccator and, after cooling, weigh.

Incinerate again at a dull red for a further five minutes. Remove in the desiccator and reweigh.

Continue this treatment till two successive weighings do not differ by more than ·0005 gm.

Calculations and Accuracy.—Let x gm. = weight **CuO**, and y gms. = weight **Cu**. Then

$$y = \frac{x \times 63{\cdot}3}{79{\cdot}3} = \text{the weight of Cu present.}$$

The percentage of **Cu** is found as follows:—

Let m gms. be the weight of the salt taken

$$\text{Then the percentage of Cu} = \frac{y \times 100}{m}$$

Or combining the calculations,

$$\text{The percentage of Cu} = \frac{x \times 63{\cdot}3 \times 100}{79{\cdot}3 \times m}$$

The result can be most quickly calculated by logarithms.

Regarding the accuracy of this method few exact data seem to be available, probably for the reason that the method is rather tedious, and is replaced in practice by the cyanide, iodide, or electrolytic methods, which are applicable to both salts and complex ores.

THE ESTIMATION OF LEAD IN LEAD NITRATE, $Pb(NO_3)_2$.

Apparatus, Chemicals, etc.—As usual. For analysis the student may procure a sample of the salt labelled "pure for analysis." If this is not available, the student may prepare some by dissolving litharge in nitric acid and crystallising out the nitrate, which is then purified by recrystallisation.

Method, Reactions, etc.—The method here employed gives further practice in manipulation, and at the same time is capable of yielding very accurate results. The lead in solution is precipitated according to the equation,

$$Pb(NO_3)_2 + H_2SO_4 = \underline{PbSO_4} + 2HNO_3$$

Lead sulphate being formed as a white powder, which is practically insoluble in E. H_2SO_4, but is more soluble in a mixture of HNO_3 and H_2SO_4, hence any HNO_3 must be removed by evaporation, and the residue again taken up with E. H_2SO_4. As the precipitate is slightly soluble in water but insoluble in alcohol, the latter is used for washing. The precipitate on ignition is unchanged at a red heat, but at a white heat gives off SO_3. As any precipitate adhering to the paper is easily reduced by the carbon on incineration, a platinum wire must not be used, as the reduced lead will alloy with the platinum. The paper is first incinerated in the crucible, and the ash moistened with a drop of strong HNO_3, and then a drop of strong H_2SO_4. This converts any reduced lead to nitrate, and then to sulphate. The precipitate is then incinerated as usual.

Details of the Analysis.—As $Pb(NO_3)_2$ contains a high percentage of lead, weigh out about ·5 gm. of the salt and transfer it to a 200 c.c. beaker. To the beaker add 20 c.cs. distilled water, and gently heat till the nitrate is dissolved. Add 5 c.cs. E. H_2SO_4, and evaporate down nearly to dryness till white fumes come off. Care must be taken in regulating the heat, so that the solution does not spit. Any HNO_3 has now been expelled. Remove the beaker and, when nearly cool, add 50 c.cs. E. H_2SO_4 and 100 c.cs. of good methylated or rectified spirit.

Transfer the precipitate and liquid to the filter, slightly agitating before pouring, so as to remove the heavy precipitate. Wash the last of the precipitate on to the filter with methylated spirit, and wash the precipitate and filter free from H_2SO_4 by a number of small washes of methylated spirit. Test a little of the washings for sulphuric acid by means of $BaCl_2$.

When thoroughly washed, lightly cover and remove to the drying oven.

When dry, remove the precipitate from the filter on to a piece of glazed paper and cover it with a glass funnel. Roll up the paper precipitate-side in, place it in a weighed crucible and gently burn off the carbon, and incinerate till a grey ash remains. On this ash let fall one drop of strong HNO_3 and one drop of strong H_2SO_4. Gently heat to expel the excess of these acids. Now transfer the precipitate from the glazed paper to the crucible, brushing down any adhering particles with a fine camel's-hair brush. Incinerate the combined precipitate and ash for ten minutes at a dull red heat. Remove in a desiccator, and when cool weigh. Repeat the incineration and weighing till the weight is constant within the limits of ·0005 gm.

Calculations and Accuracy.—Let x gms. = the weight of $PbSO_4$ found, and let y gms. = the weight of Pb in x gms. of $PbSO_4$. Then

$$y = \frac{x \times 207}{303}$$

Let m gms. = the weight of salt taken.

Then the percentage of lead is calculated thus,

$$\text{Percentage lead} = \frac{y \times 100}{m}$$

Or combining the calculations,

$$\text{Percentage lead} = \frac{x \times 207 \times 100}{303 \times m}$$

The results obtained from duplicate estimations should agree within $\frac{1}{10}$th of a per cent. For example, two results may give 68·16% and 68·24% lead. The accuracy attainable by this method is high, and justifies its inclusion amongst the methods previously classed as good.

This method will be again used in the analysis of galena, and in a modified form it will be given under Volumetric Analysis, where its application to the separation of lead in complex substances will be considered.

THE ESTIMATION OF CHLORINE IN SODIUM CHLORIDE, NaCl.

Apparatus and Chemicals.—As usual. The student may take for analysis a sample of the pure salt, or if that be not at hand the commercial chloride may be purified by passing HCl gas (which has been washed in strong HCl) through a saturated solution of the salt, when, by change of solvent, the sodium chloride is precipitated as a crystalline powder, which is separated from the liquor, and any traces of water and hydrochloric acid are removed by heating in a porcelain dish.

Method and Reactions.—In the method employed the chlorine is precipitated from the solution of NaCl by the addition of $AgNO_3$, the reaction being shown by the equation—

$$NaCl + AgNO_3 = \underline{AgCl} + NaNO_3$$

On incineration after drying, the precipitate is readily reduced by the carbon of the filter paper; therefore a platinum wire must not be used for incinerating the paper, unless special care is taken that none of the reduced silver comes in contact with the wire.

In the precipitation a little free HNO_3 is added to the solution, as AgCl is less soluble in a solution of $NaNO_3 + HNO_3 + H_2O$ than in one of $NaNO_3 + H_2O$.

Details of the Analysis.—Weigh out about ·25 gm. of the pure dry salt and transfer it to a 200 c.c. conical beaker.

To the contents of the beaker add 50 c.cs. distilled water to dissolve the salt. Then add 1 c.c. 5E. HNO_3. Now gradually add $\frac{E}{5}$. $AgNO_3$, stirring and letting the precipitate settle between each addition. If no fresh precipitation (as indicated by a milkiness where the two liquids meet) occurs, the chlorine has been completely precipitated as silver chloride. Heat the contents of the beaker nearly to boiling. Remove and let settle.

Wash the precipitate several times by decantation on to the filter, using as a wash distilled water acidified with HNO_3 (about 1 c.c. 5E. HNO_3 in every 50 c.cs. distilled water will answer).

The washing must be continued till no reaction is obtained on testing about 1 c.c. of the washings (as they drop from the funnel) with a drop of HCl.

The funnel and paper are removed and dried in the oven as usual.

Several methods of treating the precipitate and paper are available, and the student will find them given in the higher text-books. He will obtain good results as follows:—

Heat strongly and weigh a small porcelain (not platinum) crucible and lid. Remove as much as possible of the precipitate from the paper and transfer the precipitate to the crucible. Set the lid on the pipeclay triangle and tripod placed on a piece of glazed paper. Carefully fold the paper and pass a rather stout platinum wire through the top edges of the folded paper, and with a low bunsen flame gently incinerate the paper over the porcelain lid. When grey, deposit any ash left on the wire on to the lid, and moisten the ash with one drop of strong HNO_3, and then with one drop of strong HCl, any reduced silver being changed to nitrate, and then to chloride. Carefully heat the lid to drive off the excess of acid. Remove it to the desiccator. The crucible and precipitate are now heated till the silver chloride just begins to melt, and are then removed to the desiccator, and when cool the crucible lid and precipitate are weighed.

The crucible may be cleaned by adding a little E. H_2SO_4 and a small piece of zinc. The chloride is thus reduced, and the adhering mass is easily detached from the crucible.

Calculations and Accuracy.—Let x gms. = the weight of AgCl found, and let y gms. = the weight of chlorine contained in y gms. of AgCl.

$$\text{Then } y = \frac{x \times 35{\cdot}5}{143{\cdot}5} \text{ gms.}$$

Let m gms. = the weight of salt taken.

Then the percentage of chlorine is calculated thus—

$$\text{Percentage chlorine} = \frac{y \times 100}{m}$$

Or combining the calculations,

$$\text{Percentage chlorine} = \frac{x \times 35{\cdot}5 \times 100}{143{\cdot}5 \times m}$$

The results obtained by this method fully justify its inclusion amongst the most accurate methods. The accuracy of an analytical gravimetric method depends largely on the insolubility of the precipitate in the liquid (menstruum). For detailed information regarding the solubility of precipitates, Comey's *Dictionary of Chemical Solubilities* may be consulted. Regarding the completeness of the precipitation, the same authority may be consulted, more especially as regards the effects of varying temperature and other conditions.

THE ESTIMATION OF SO_4 IN COPPER SULPHATE.

$CuSO_4 5H_2O$.

Apparatus, Chemicals, etc.—As usual. The student may take for analysis another portion of the salt used in the estimation of copper.

Method and Reactions.—Briefly, the SO_4 is precipitated as a fine powder by a solution of barium chloride thus—

$$CuSO_4 + BaCl_2 = \underline{BaSO_4} + CuCl_2$$

Notwithstanding the apparent simplicity of the reaction, several points must be carefully noted as essential to accuracy.

If the precipitation be carried out in a cold solution and is filtered at

once a very fine precipitate which will pass through the filter is obtained, and a clear filtrate is more readily secured if HCl or NH_4Cl be present. If, then, HCl be added for this purpose, the quantity added must be so chosen that the least possible quantity of $BaSO_4$ is dissolved, for $BaSO_4$ is appreciably soluble in dilute acids. Some difference of opinion exists as to the best conditions. "Blair" advocates 2 c.c. 10E. HCl (free acid) in a bulk of 100 c.cs. as the best conditions, and recommends precipitation at the boiling point. The student may follow these instructions, and if time permits he may refer to other authorities.

The usual precaution of treating the ash with acid to reconvert any reduced products into sulphate must be taken.

These few remarks should further impress on the student the necessity of carefully considering and following the minutest detail. It may be that such details are not perfect, or are even wrong, but in the present state of the science they must, as a rule, be accepted as the best available, and should be conscientiously followed by the student.

Details of the Analysis.—Weigh out as before from the weighing tube about ·5 gm. copper sulphate and transfer it to a 200 c.c. beaker.

To the contents of the beaker add 100 c.cs. of distilled water, and gently heat till the copper sulphate is all dissolved. Now add 2 c.cs. of 10E. HCl and heat to boiling.

In a small beaker heat to boiling about 10 c.cs. E. $BaCl_2$, and add a little at a time with constant stirring the E. $BaCl_2$ till the precipitation is complete (on setting, a few drops more of the $BaCl_2$ must produce no milkiness). Any large excess of the reagent must be avoided.

The precipitate on settling is now washed several times by decantation, and is then transfered to the filter and washed till the washings give no reaction on being tested for chlorine.

Remove the funnel and filter to the drying oven and dry as usual.

When dry, the precipitate is transferred to a weighed crucible, and the paper is ignited on a platinum wire, and the ash dropped on a clear space on the bottom of the crucible, prepared by gently tapping the crucible so that the precipitate moves to one side. The ash is moistened with one drop of strong HCl and one drop of strong H_2SO_4. The crucible and contents are then gently heated to expel excess of acid, and are then heated to a red heat for fifteen minutes, placed in the desiccator, cooled and weighed as usual, the process being repeated till the weight is constant within the required limits.

Calculations and Accuracy.—Let x gms. = the weight of $BaSO_4$ found, and y gms. = the weight of SO_4 in x gms. $BaSO_4$.

$$\text{Then } y = \frac{x \times 96}{233} \text{ gm.}$$

Let m gms. = the weight of salt taken.

Then the percentage of SO_4 is calculated thus:—

$$\text{Percentage } SO_4 = \frac{y \times 100}{m}$$

Or combining the calculations,

$$\text{Percentage } SO_4 = \frac{x \times 96 \times 100}{233 \times m}$$

When care is taken regarding the exact conditions of precipitation this method yields accurate results, and will be met with again, when its accuracy in the presence of certain other elements will be noticed

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THE ESTIMATION OF CHROMIUM IN POTASSIUM BICHROMATE $K_2Cr_2O_7$.

Apparatus, Reagents, etc.—The usual equipment, with the addition of either a 'syphon' of liquid SO_2, or a flask arranged for the generation of SO_2 by means of copper and sulphuric acid, a wash bottle being inserted between the gas supply and the gas delivery tube.

As the purified salt is easily obtained, the student may conduct the analysis on this material.

Method and Reactions.—The chromium in 'chromic' salts is precipitated by ammonia as the hydrate $Cr_2(HO)_6$, which on incineration yields the oxide Cr_2O_3 and H_2O.

In a solution of $K_2Cr_2O_7$, however, the chromium is not in the chromic state, therefore the first step in the analysis is to reduce the 'bi-' or 'di-chromate' to this state. The reducing agent here used is sulphur dioxide in the gaseous state. The SO_2 is oxidised to SO_3, forming sulphuric acid at the expense of the oxygen of the chromate, chromic sulphate being formed, which colours the liquid green.

The following equations represent the changes taking place:—

$$2CrO_3(+K_2O) = Cr_2O_3(+K_2O) + O_3$$
$$3SO_2 + O_3 = 3SO_3$$
$$Cr_2O_3 + 3SO_3 = Cr_2(SO_4)_3$$

Then on adding ammonia to this solution after boiling off the excess of SO_2,

$$Cr_2(SO_4)_3 + 6NH_4HO = \underline{Cr_2(OH)_6} + 3(NH_4)_2SO_4$$

and on incineration

$$Cr_2(OH)_6 = Cr_2O_3 + 3H_2O$$

and as chromic oxide (Cr_2O_3) is not easily reduced at a red heat by the carbon of the filter paper, the precipitate and paper may be incinerated together.

Details of the Analysis.—Weigh out about ·5 gm. of the salt and transfer it to a 200 c.c. beaker of a deep narrow form, to allow of quick reduction by the sulphur dioxide. To the salt add 100 c.cs. distilled water and dissolve it without the aid of heat (gas is more soluble in a cold than in a hot solution).

The gas supply is so regulated that a gentle stream of SO_2 is delivered. The glass delivery tube dips to the bottom of the beaker, and the top is nearly covered with a small clock glass to prevent loss by the gas bubbles throwing small quantities of the liquid over the side. On passing the gas the colour of the liquid gradually changes from yellow to green, and the reduction is complete when no yellow tinge is visible on swirling a little of the liquid up the side of the beaker.

The solution is now warmed till the excess of SO_2 present is removed. This point may be ascertained by cautiously smelling the escaping vapour. 5E. NH_4HO is now carefully added, with gentle stirring, till in excess, as ascertained by removing a drop on a glass rod and testing it on red litmus paper. The contents of the beaker are now boiled to expel any excess of ammonia, as detected by smelling the escaping vapour. Allow the precipitate to settle, and wash it two or three times by decantation with boiling water, and then transfer the precipitate to the filter until the washings give no reaction for sulphates. Remove the funnel and contents to the drying oven and dry as usual.

When dry, remove the paper and contents and transfer them to a weighed crucible, folding in any overhanging filter paper. Gently ignite until the paper has ceased flaming, and then proceed with the incineration at a red heat for 15 minutes, gently stirring with a glass rod, or better, a stout platinum wire, to expose any unburnt carbonaceous matter to the action of the air.

Remove the crucible and contents in the desiccator, cool and weigh. Repeat till constant within the required limits.

Calculation, Accuracy, etc.—Let x gms. = the weight of Cr_2O_3 found, and y gms. = the weight of Cr in x gms. Cr_2O_3

$$\text{Then } y = \frac{x \times 104}{152} \text{ gms.}$$

Let m gms. = the weight of salt taken.

Then the percentage of Cr is found thus—

$$\text{Percentage Cr} = \frac{y \times 100}{m}$$

Or combining the calculations—

$$\text{Percentage Cr} = \frac{x \times 104 \times 100}{m \times 152}$$

Provided the reduction has been thorough, satisfactory results may be obtained by this method, as the precipitate is only very slightly soluble in the liquid present.

THE ESTIMATION OF WATER OF CRYSTALLISATION IN COPPER SULPHATE, $CuSO_4,5H_2O$.

Apparatus, Reagents, etc.—As usual, the student may take for analysis the purified salt formerly used, as the results here obtained form a check on his previous work.

Method, Reactions.—On heating $CuSO_4,5H_2O$ at 100° C. it is converted into $CuSO_4,H_2O$ which is a bluish white salt, and on further heating at 240° C. this salt becomes anhydrous.

As the anhydrous salt is very hygroscopic, care must be taken that between the drying and the weighing no moisture is absorbed. To attain this end the salt is dried on one of two accurately fitting watch glasses, and when removing the dried salt from the oven the other glass is immediately clamped on and the clamped glasses placed in the desiccator.

Details of the Analysis.—Dry two watch glasses and a clamp in the air oven at 120° C. and place in a desiccator and weigh. Unclamp the glasses, and from the weighing tube or bottle shake in about 1 gm. of the salt. Clamp the glasses and reweigh to ascertain the weight of the salt taken.

Unclamp the glasses and transfer them to the air oven and heat at 120° for half an hour, and then raise the temperature to 250° C. and continue the heating for half an hour. Clamp quickly. Place in the desiccator, and when cool weigh quickly, the approximate weights having been calculated and placed on the pan before removing the glasses and salt from the desiccator.

Unclamp the glasses and transfer quickly back to the oven and heat again for another half-hour. Clamp, place in the desiccator, cool and

reweigh. The salt cannot be considered as perfectly dehydrated until the weighings at successive half-hours are constant within ·0005 gm.

Calculation, Accuracy.—Let x gms. = the difference between the weight of salt taken and the final weighing when thoroughly dehydrated. Let m gms. = the weight of salt taken.

$$\text{Then percentage } H_2O = \frac{x \times 100}{m}$$

The accuracy of the results may be checked by calculation from the formula

$$249 \text{ parts } CuSO_4,5H_2O \text{ contain } 90 \text{ parts } H_2O \text{ or } \frac{90 \times 100}{249} \%$$

The results obtained in the estimations of Cu and SO_4 will give an extra check on the results obtained in this estimation.

Supplementary Direct Method.—In the method just given the water is estimated by *loss* on heating. If time be available, the student may check the results so obtained by the following.

Method, Reactions, etc. — The salt is dehydrated by heating and the expelled water of crystallisation is absorbed in a weighed quantity of dry calcium chloride. The additional weight represents the water absorbed.

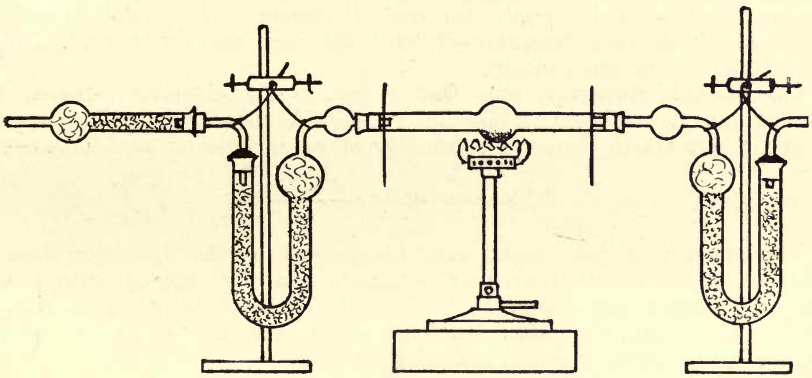


Fig. 61.

Apparatus, Reagents, etc.—The apparatus as shown in fig. 61 must be procured and fitted together. Procure two calcium chloride tubes (15 cm. deep and 1·5 cm. diameter). Thoroughly dry them and insert a loose plug of cotton-wool down the wide limb of each, and by suction draw it up into the large bulb. Then fill each tube as shown with dry calcium chloride in pieces about the size of a barley grain. Fit the wide ends with corks bored to carry the connecting tubes shown. Cut the corks flush with the tops of the tubes, and cover the top of each cork with sealing-wax to prevent it absorbing moisture from the air. Fill the guard tube on the left in the same way, connecting it to one of the chloride tubes as shown. The guard tube may be replaced by a small wash bottle or set of bulbs containing 36E. H_2SO_4. Procure a tube of hard glass with a bulb blown in the middle and of the proportions shown. Fit each end with a cork bored to receive the connections shown. A piece of thin asbestos board is fitted on each end to shield the corks and tubes from the direct heat of the burner. Provide some means of aspirating a steady current of air whilst the salt is

being heated. Before proceeding to the analysis connect the apparatus, heat the bulb, and pass a current of air for about 10 to 15 minutes.

Details of the Analysis.—From the weighing tube shake out approximately 2 gms. of the salt into the tip of the trough of a V-shaped piece of stiff paper, sufficiently long and narrow to reach into the ignition bulb. By this means transfer the salt into the ignition bulb, taking care that none is deposited elsewhere.

Reweigh the weighing tube to ascertain the weight of salt taken. Detach the chloride tube on the left from the guard tube and the ignition tube. Carefully wipe its exterior with a soft dry linen cloth, having previously closed its open ends by small pieces of rubber tubing and short lengths of glass rod. In this tube the water of crystallisation is to be absorbed. Carefully weigh the tube, and then reconnect it to the guard tube and the ignition tube. The guard tube protects the chloride tube from the moisture of the atmosphere, and the second chloride tube on the right absorbs any moisture from the air aspirated through the tubes.

Connect the aspirator to the guard tube and draw a *gentle* current (two or three bubbles per second) of air through the tubes, and at the same time *gently* heat the bulb of the ignition tube with a low flame from a rose bunsen. Continue the low heat till the salt becomes much lighter in colour, then increase the heat gradually till the salt becomes perfectly white. Remove the heat and aspirate till cool. Disconnect the weighed chloride tube, closing its ends immediately with the caps previously used. Wipe the tube as before and reweigh.

Calculations, Accuracy, etc.—Let x gms. = the difference between the first and second weighings of the calcium chloride tube, and let m gms. = the weight of salt taken, then the percentage of water is found as follows:—

$$\text{Percentage water} = \frac{x \times 100}{m}$$

The accuracy of this method may be checked by the theoretical calculation and by the results previously obtained. In the case of certain salts such as hydrated carbonates, the first method cannot be used, as CO_2 is evolved in addition to water. In this and other like cases the second method, with certain modifications, may be used.

Concluding Remarks.

The student has now performed some seven or eight simple quantitative gravimetric estimations. The results and manipulation must be closely supervised by the demonstrator, and no student should proceed further until he has conscientiously and successfully performed the foregoing estimations. As these estimations have all been conducted on 'chemically pure' compounds, the student has a ready means of checking the accuracy of his work.

The aim of the student at this stage should be the attainment of **accuracy.** Though his progress may be somewhat slow, it is useless aiming at speed until accuracy is secured, and to attain this accuracy it is repeated here that *the only road is strict attention to the minutest detail.*

For the present the treatment of gravimetric methods stops here, but will be taken up again when dealing with what may be called 'Mixed Analyses.' In these so-called 'mixed analyses' certain elements are determined gravimetrically, some volumetrically, and some by electrolytic methods.

Naturally, then, before attempting these analyses of complex substances (*e.g.* silicates, complex sulphide ores, etc.), some practice in volumetric

and electrolytic methods is necessary. It is true that these substances could be analysed by gravimetric methods alone, but at the sacrifice of much time; and as this is primarily a text-book for the use of the metallurgical student, to whom time now, and more especially in his future career, is an item of value, gravimetric methods that can be replaced by more speedy volumetric methods of sufficient accuracy will not be considered. In the next two chapters volumetric and electrolytic methods will be considered, and following them certain typical examples of mixed analyses.

CHAPTER V.

VOLUMETRIC ANALYSIS.

Introductory.

In gravimetric analysis a certain quantity of a substance was weighed out, and by certain operations a precipitate of known composition was obtained and accurately weighed. In volumetric analysis a certain quantity of the substance is weighed out, but the substance sought is estimated by noting the *volume of reagent of known strength* added to bring about some chemical reaction such as precipitation, oxidation, reduction, or neutralisation.

Two *units* are here used—*one gram* and *one cubic centimetre*. The former unit has been considered; some explanation will now be given of the latter. For further information on this and other points connected with volumetric analysis, the student is referred to Sutton's standard work on the subject.

The true c.c. contains one gm. distilled water at 4° C., but as this is an inconvenient working temperature, chemists have adopted temperatures of 15° C., 16° C., and 17·5° C. It will be found advisable, as suggested by Sutton, to follow the middle course, and take the **unit, as one c.c. contains 1 gm. distilled water at 16° C.** Any other unit may be adopted provided all the instruments (flasks, pipettes, burettes) are graduated alike, that is, are *relatively* accurate.

If measuring solutions at other temperatures than 16° C. the volume at this temperature may, if required, be ascertained from the following table prepared by Casamajor. The example following shows its application.

Normal Temperature, 15° C.

– represents contraction, + represents expansion.

Deg. C.		Deg. C.		Deg. C.	
7	– ·000612	20	+ ·000841	33	+ ·004035
8	– ·000590	21	+ ·001039	34	+ ·004342
9	– ·000550	22	+ ·001246	35	+ ·004660
10	– ·000492	23	+ ·001462	36	+ ·004987
11	– ·000420	24	+ ·001686	37	+ ·005323
12	– ·000334	25	+ ·001919	38	+ ·005667
13	– ·000236	26	+ ·002159	39	+ ·006040
14	– ·000124	27	+ ·002405	40	+ ·006382
15	Normal	28	+ ·002657		
16	+ ·000147	29	+ ·002913		
17	+ ·000305	30	+ ·003179		
18	+ ·000473	31	+ ·003453		
19	+ ·000652	32	+ ·003739		

Thus if 40 c.cs. solution have been read off at 32° C. the table states that 1 c.c. water at 15° C. becomes 1·003739 c.cs. at 32° C.

$$\text{Hence } 40 \text{ c.cs. at } 32^\circ \text{ C.} = \frac{40}{1{\cdot}003739} \text{ c.cs. at } 15^\circ \text{ C.}$$
$$= 39{\cdot}85 \text{ c.cs. at } 15^\circ \text{ C.}$$

Or in other words, if a solution at 32° C. be used in a burette standardised at 15° C., and the solution were made up at 15° C., then the reading obtained was ·15 c.cs. too much; that is a percentage error of

$$\frac{100 \times {\cdot}15}{39{\cdot}85} = \frac{15}{39{\cdot}85} = {\cdot}38\%$$

The same table may be used for the 16° standard. This table cannot be applied to solutions of acids and salts. These substances, as a rule, expand more rapidly than water, hence the error introduced will be larger than with water.

MEASURING APPARATUS.

Having considered briefly the units of measurement to be employed, the necessary apparatus will now be described.

(*a*) **Units of weight.**—The balance and weights as before described are here used.

(*b*) **Units of volume.**—For the student's purposes the following outfit will suffice:—One 1000 c.c. graduated 'test-mixer,' one measuring flask 1000 c.c., one measuring flask 250 c.c., one or two 50 c.c. burettes, preferably with glass stopcocks and divided into tenths of a c.c.; pipettes 25 c.c., 50 c.c., and one graduated.

Before proceeding to standardise these instruments, the student must see that they are thoroughly clean.

If slightly greasy, the water runs down unevenly on the sides, giving inaccurate results. Such apparatus should be rinsed with dilute soda solution, and if this fails, recourse must be had to a cleaning solution of strong H_2SO_4 and $K_2Cr_2O_7$. The cleansing reagent must be completely removed, and the apparatus finally washed with distilled water.

Calibrating the Measuring Vessels.—It is required that

(*a*) The graduations on a vessel agree with one another.

(*b*) The graduations on one vessel agree with those on another vessel.

1. To calibrate the Burette.—The burette, as will be seen from fig. 62, is a long straight glass tube, terminated at its lower end by a glass stopcock and jet, or by a rubber tube, jet, and pinchcock. The tube is graduated, and must be fixed *vertically* in a stand as shown. The stopcock is closed and a small funnel is inserted in the upper end, and distilled water at 16° C.

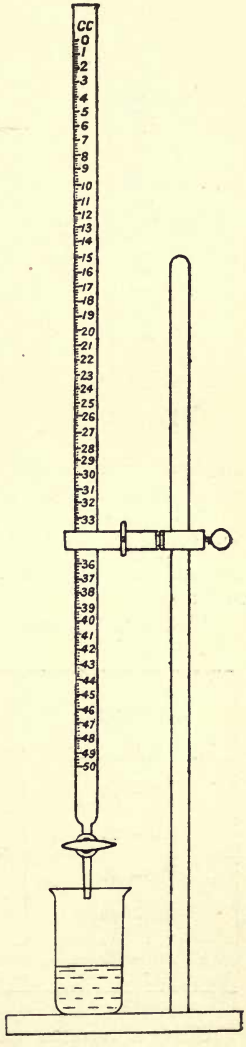


FIG. 62.

is poured in till it rises to the zero mark. When reading the volume of water always observe the following rules:—

(*a*) The time between the escape or pouring in of a liquid and the reading should be constant.

(*b*) The eye should be in a line with the surface of the liquid as at *a*, fig. 63 (not *b* or *c*).

(*c*) The same portion of the meniscus should always be read.

Figs. 64 and 65 show other methods of reading the volume. Rule *a* applies to both of these. Rules *b* and *c* apply partially. In fig. 64 the Erdmann float is shown, and with it the eye should be so placed that the etched circle on the float appears as a straight line. When using the Schellbach burette the eye must be so placed that a defined point is obtained, as in fig. 65.

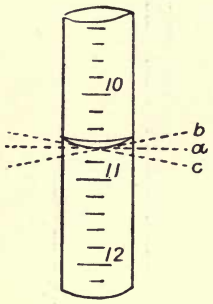


FIG. 63.

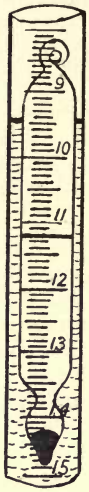


FIG. 64.

FIG. 65.

If the water does not stand exactly at zero, adjust its level to that point by filling or drawing off as may be necessary. The temperature of the room and apparatus should be about 16° C. (61° F.).

The graduation of the burette is now checked thus:—

Clean a 100 c.c. flask with distilled water, finishing with alcohol. Warm till perfectly dry. Cool, wipe, and weigh, with a small watch glass on top as a cover.

Remove the watch glass. Place the flask under the burette on a clean piece of dry paper. Run in exactly 10 c.cs. Cover and reweigh. Run in another 10 c.cs. and weigh again, and so on till the burette is emptied to the lowest mark (50).

Tabulate the results as follows:—

Graduation.	Weight Flask.	Weight Flask + Water.	Weight Water.
0 – 10	11·4320 gms.	21·4418 gms.	10·0098 gms.
10 – 20	,,	31·4520 ,,	10·0102 ,,
20 – 30	,,	41·4498 ,,	9·9978 ,,
30 – 40	,,	51·4602 ,,	10·0104 ,,
40 – 50	,,	61·4664 ,,	10·0062 ,,

Since a burette can only be read to $\frac{1}{10}$th of a cubic centimetre, it is useless reading the weights past the second decimal place; and if for any 10 c.cs. the

error is not greater than ·02 gm. $\left(\frac{2}{100}\text{ of }10 = \frac{1}{500}\text{th error, or }\cdot 2\%\right)$, then the burette may be used. If the deviations vary considerably, then the student must either obtain a better burette or draw out in his note-book a scale of corrections, placing opposite 1 c.c. $\frac{1}{10}$th the weight of the first 10 c.cs.; opposite 2 c.cs., $\frac{2}{10}$ths, and so on up to 10 c.cs.; opposite 11 c.cs. place the corrected value of 10 c.cs. plus $\frac{1}{10}$th the weight of the second 10 c.cs., and so on.

For the student's purposes, the relative accuracy of the various instruments and their graduations alone need be considered fully. If 10 c.cs. do not weigh exactly 10 gm. at 16° C., this fact does not in any way prohibit the use of the burette, so long as each successive 10 c.c. portion has the same value, and also so long as the burette agrees with the pipette and other measuring vessels.

FIG. 66.

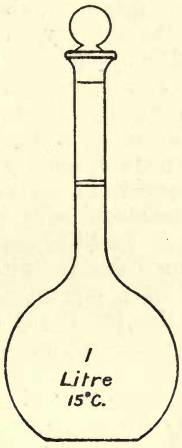
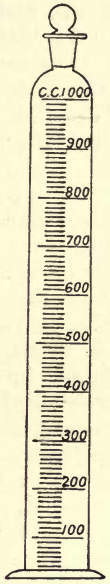


FIG. 67.



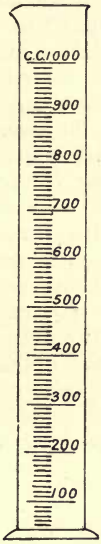


FIG. 68.

Calibrating the Pipette.—The best form of pipette is that shown in fig. 66. It is filled by applying *gentle* suction at the upper end till the liquid rises a little above the mark, covering quickly by slipping the tip of the finger over the upper end, gently easing the finger so as to allow the liquid to run down till the bottom of the meniscus coincides with the mark. Clean, dry, and weigh the flask before used. Fill the pipette with distilled water at the same temperature as before. Remove any hanging drop. Bring the tip of the pipette against the inner side of the neck of the flask and let the pipette empty into the flask, allowing it to drain thirty seconds after emptying. (It is important that the pipette should always be emptied in the same way, allowing the same time to drain.)

Reweigh the flask and water, and compare the figures thus obtained with the corrected value of 25 c.cs. on the burette. As a check, set the water in the burette at the 50 c.c. mark, and empty the pipette twice into the burette. The level should now closely coincide with the zero mark.

Calibrating the Flasks.—The form of flask used is shown in fig. 67. The

accuracy of a 250 c.c. flask may be checked either by weighing or carefully delivering ten quantities of 25 c.cs. each from the checked pipette. This latter operation must be repeated till the results are uniform. The 1000 c.c. flask may be checked by weighing or by filling four times from the 250 c.c. flask. In every case where a liquid is delivered from a vessel, due time must be allowed for the liquid to thoroughly drain from the walls of the vessel.

In fig. 67 two marks are shown. The flask is filled to the upper mark for 'pouring' and to the lower for 'standardizing.'

The 'test-mixers' may be calibrated in a similar way.

General Remarks.—When finished with, all apparatus should be thoroughly cleaned and put away. Burettes may be set aside filled with distilled water, which is drained off when the burette is to be used again. The burette is then washed with a little of the solution to be used, the washings being drained off, the stopcock closed, and the burette filled as usual by the funnel. As a rule, it should be filled a little above the zero mark, as a few c.cs. may require to be run off to displace any air bubbles that may have collected about the jet.

Before reading the burette, time must be given for the liquid to drain down the walls. The student must get into the habit of performing all such measurements under similar conditions. Before making a final reading, at least 30 seconds should elapse between the delivery and the reading.

All solutions used in a burette should be thoroughly shaken to secure even mixing before transference to the burette or other measuring vessel.

If a solution has to be made up to, say, 1000 c.cs., the substance is dissolved in a small quantity of the solvent in a beaker. When cool, this solution is poured down a glass rod through a small funnel into a 1000 c.c. measuring flask. The beaker is then washed out several times with distilled water (or other wash as required), the washings being poured down the glass rod through the funnel into the flask. Distilled water is now cautiously added till the lower edge of the meniscus coincides with the mark.

If salts crystallise out on the point of a pipette, they must be removed before using the pipette again. If on the jet of the burette, the deposit is removed by wiping, one or two c.cs. of the liquid are run off, and then the burette is ready for re-use.

Always use a funnel for filling the burette, and when full remove the funnel, rinse and dry it, and it is ready for re-use. In brief, exercise your intelligence in avoiding anything that may in any way vitiate your results. The remarks previously made about cleanliness apply again here.

General Principles.—In every volumetric analysis it is necessary that we know—

1. The value of one c.c. of the solution measuring the reaction.
2. The exact point (end point) at which the reaction is complete.

If, for instance, the percentage of H_2SO_4 in a given solution is to be determined, this may be done by adding a solution of NaOH till the liquid is *just* neutral. Assuming that 12 c.cs. NaOH solution were required, this information clearly is of little use unless we know the strength of each c.c. of NaOH; that is, what fraction of a gram of H_2SO_4 each c.c. of NaOH solution can neutralise. Therefore such solutions must have their value, in regard to the substance sought, determined. This process is termed '**standardisation,**' and solutions thus checked are termed '**standard solutions,**' and when the standard solution contains an 'equivalent' proportion of the active agent it is termed a '**normal solution.**' Briefly, a normal solution may be defined as a solution one litre of which at 16 °C. contains a number of grams of the active agent chemically equivalent to one atom of hydrogen.

In other words, a '**normal solution**' of any salt acid or other substance is simply an '**equivalent solution**'; briefly an **E. solution.**

E.g.—A normal solution of H_2SO_4 contains $\frac{2+32+64}{2} = 49$ gms. H_2SO_4 per litre as it contains two replaceable H atoms.

Similarly a normal solution of oxalic acid, $H_2C_2O_4,2H_2O$ contains $\frac{2+24+64+36}{2} = 63$ gms. per litre.

A normal solution of HCl contains $\frac{1+35{\cdot}5}{1} = 36{\cdot}5$ gms. per litre, there being only one replaceable H atom. And so on.

It must be remembered, however, that the special use to which the solution is to be put must always be considered. For instance, if $K_2Cr_2O_7$ is used as a precipitating reagent, thus,

$$2Ba(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O = \underline{2BaCrO_4} + 2KC_2H_3O_2 + 2HC_2H_3O_2$$

one molecule of $K_2Cr_2O_7$ precipitates two atoms of Ba, each of which is equivalent to two atoms of H, hence the normal solution of $K_2Cr_2O_7$ for this purpose contains $\frac{78+104+112}{4} = 73{\cdot}5$ gms. per litre.

But if used as an oxidising agent it splits up thus,

$$K_2Cr_2O_7 = K_2O + Cr_2O_3 + O_3$$

and each atom of O is equivalent to two atoms of H, therefore a normal solution for this purpose will contain $\frac{78+104+112}{6} = 49$ gms. (nearly) per litre.

Similarly, $K_2Mn_2O_8$ yields five atoms of O, hence the normal solution contains 31·5 gms. per litre.

Solutions other than normal, or simple fractions of normal, are sometimes used, and are termed *empirical solutions*, and will be noticed later on.

A normal solution is frequently too strong for accurate work, hence weaker solutions of $\frac{1}{2}$, $\frac{1}{10}$, $\frac{1}{100}$ this strength, termed *semi*,- *deci*,- and *centi-normal* respectively, are used.

The amount of material taken for analysis and the strength of standard solution should so agree that about 40 c.cs. of the standard solution are required to complete the reaction.

The determination of the *end point* of a reaction is a matter of much importance. Some visible indication must be given at the exact moment of completion of the reaction. This visible indication manifests itself in various ways, the following being the chief:—

1. **Cessation of Precipitation.**
2. **First Formation of a Permanent Precipitate.**
3. **Change in Colour of the Solution treated.**
4. **Changes produced by 'Indicators.'**

Regarding the first three indications nothing need be stated here, as they will, when treated of, be quite intelligible to the student with a sound training in theoretical chemistry, but concerning the use of 'indicators' a little explanation is necessary. For information on the theory of indicators

the student is referred to the works of "Ostwald," "Nernst," and "Walker" on physical chemistry.

An Indicator may be defined as a substance (used in volumetric analysis) which, by change in colour or other visible change, indicates or determines the exact point at which a given reaction is complete.

The following are some of the chief indicators in use:—

(*a*) **Litmus Solution.**—Crush about 5 gms. of the commercial litmus. Add about 20 c.cs. of water, boil and decant. Add further quantities of water, repeating the boiling till about 100 c.cs. of solution are obtained. Take about 1 c.c. of the liquid in a test tube and add 1 drop of *very dilute* acetic acid, and the blue changes to violet and then to red. Now to the bulk of the solution add very cautiously, drop by drop, very dilute acetic acid till the neutral point indicated by the violet colour is reached. Before use the solution should always be of this tint. A few drops of chloroform added prevent the formation of mildew. Preserve the solution in a *loosely* stoppered bottle.

As an experiment, transfer 2 c.cs. litmus solution to a clean beaker containing about 100 c.cs. distilled water. Add a few drops H_2SO_4; note the colour. Now add NH_4HO drop by drop and note the change of colour.

This indicator must not be used with alkaline carbonates, as these, when acted on by acids, liberate free CO_2, in the presence of which (in cold solutions) litmus is not reliable. When used at night-time the colour changes are best seen by yellow monochromatic light, obtained by inserting a piece of pumice saturated in salt in a bunsen flame.

(*b*) **Methyl Orange.**—If prepared from pure materials, this indicator is of a bright orange colour and is readily soluble in water. Dissolve about ·1 gm. in 100 c.cs. water. Bottle and label. As an experiment, add 2 drops to about 100 c.cs. distilled water. Add 1 drop H_2SO_4 and the colour changes to a pink red. Now add NH_4HO drop by drop and note the change of colour.

This indicator, unlike litmus, is unaffected by CO_2, H_2S, HCN and certain other acids. As a rule, it can be used only with mineral acids; not with organic acids nor with nitrous acid or nitrites. This indicator is used in cold solutions.

(*c*) **Phenolphthalein.**—This substance is freely soluble in 60% alcohol. Dissolve ·5 gm. in 100 c.cs. of alcohol. Bottle and label.

As before, add a few drops to about 100 c.cs. distilled water and note the colour changes with acids and alkalies.

This indicator is not reliable in the presence of CO_2 or free NH_3 or ammonia salts, but it possesses one great advantage in that it can be used in alcoholic solutions, and therefore is specially suited for organic acids, many of which are insoluble in water.

Test Solutions.—When estimating ferrous salts by $K_2Cr_2O_7$ a drop of the 'assay' solution is removed on a glass rod and mixed with a drop of $K_3FeC_6N_6$ on a white porcelain plate. As long as any ferrous salt remains unoxidised a blue colour results.

Again, when precipitating the halogens with $AgNO_3$ a little K_2CrO_4 present indicates by the formation of a red precipitate that all the chlorine has been precipitated, and that the slight excess of $AgNO_3$ is forming Ag_2CrO_4 with the K_2CrO_4.

CLASSIFICATION OF METHODS OF VOLUMETRIC ANALYSIS.

The methods of Volumetric Analysis in use may be divided into five main classes:

I. **Analysis by Neutralisation or Saturation.**—Here the volume of standard solution of base or acid required to neutralise the unknown quantity of acid or base respectively is measured. This kind of analysis is termed **Acidimetry** or **Alkalimetry**, as the case may be.

II. **Analysis by Oxidation or Reduction.**—Here the volume of standard oxidising or reducing reagent required to oxidise or reduce respectively the unknown quantity of the substance sought is measured. Where iodine is the oxidising agent, this class of analysis is termed **Iodimetry**; where chlorine, **Chlorimetry**, and generally **Oxidimetry**.

III. **Analysis by Precipitation.**—Here the volume of standard precipitating reagent required to precipitate the unknown quantity of substance sought is measured.

IV. **Colorimetric Analysis.**—Here the quantity present of the substance sought is determined by comparing the colour of the solution with that of standard solutions.

V. **Gasometric Analysis.**—Here the substance sought is evolved as a gas, the volume of which is directly measured.

In the following chapters these various classes of Volumetric Analysis will be considered, and typical examples of each class will be described in detail.

The necessary calculations hardly require separate explanation, more especially as the student is accustomed to the Equivalent System of Reagents. In the details of the typical analyses the equations of the various reactions will be given and the methods of calculation briefly indicated. The student requiring further information may consult the works of Sutton and Schimpf.

The classification given above is not complete. It does not include, for instance, the well known Cyanide method for copper, which will be taken as an appendix to Class IV., although it cannot be termed, according to the usage of the term, a colorimetric method.

CHAPTER VI.

ANALYSIS BY NEUTRALISATION.

THE measurement of the strength of an acid by the quantity of alkali required to neutralise it (termed **acidimetry**), and the measurement of the strength of an alkali by the quantity of acid required to neutralise it (termed **alkalimetry**), will be considered in this chapter. The student is asked to determine volumetrically—

(*a*) The *strength* of a solution of *hydrochloric acid.*
(*b*) „ „ „ „ „ „ *ammonia.*
(*c*) The *chlorine* in $BaCl_2,2H_2O$ by treatment with known excess of Na_2CO_3 and neutralisation of the excess with standard acid.

(*a*) Determination of the Strength of a Solution of Hydrochloric Acid.

Apparatus and Reagents.—The usual volumetric and gravimetric apparatus. The student may take for analysis a sample of the ordinary bench reagent 5E. HCl. He will also require about 10 gms. pure $NaHCO_3$, and should test this substance for Cl and SO_3. If these are found, place a small plug of cotton-wool in the neck of a funnel, and on it pack about 100 gms. of the bicarbonate, and wash repeatedly with small lots of distilled water to remove the chlorides and sulphates, which are more soluble than the bicarbonate. Test the washings, and when free from these impurities spread the remainder of the salt between several folds of stout filter paper, and dry in the water oven at a temperature of 60° C., and when dry transfer to a clean weighing bottle or tube.

Method, Reactions.—A certain volume of HCl is taken at a certain temperature. Two drops of methyl orange solution are added, and the solution is 'titrated' (that is, its contents are ascertained) with a standard solution of Na_2CO_3.

$$2HCl + Na_2CO_3 = 2NaCl + H_2O + CO_2$$

The value of the Na_2CO_3 solution being known, and the volume used being also known, the strength of the HCl is easily calculated.

Preparation of the Standard Solution.—A 'normal' solution of Na_2CO_3 contains $\frac{46+12+48}{2} = 53$ gms. of the salt per litre. For the present purpose a $\frac{N.}{10}$ solution containing 5·3 gms. Na_2CO_3 per litre will answer. Weigh out about 9 gm. pure $NaHCO_3$, and transfer to a porcelain crucible which has been ignited and weighed. Heat to dull redness for fifteen minutes, stirring occasionally with a stout platinum wire or glass rod. Cool in the

desiccator and weigh, and it will be found that a little over 5·3 gms. Na_2CO_3 remain. Adjust quickly to 5·3 gms. by removing a little of the salt on the tip of a small spatula. Adjustment within ·001 gm. will suffice. If the student cannot perform this adjustment quickly, moisture will be absorbed appreciably. In such a case it will be preferable to note the exact weight of Na_2CO_3, omit the adjustment, and allow for the difference by calculating the volume of solution. If, for example, 5·4521 gms. Na_2CO_3 are present, make up to $\frac{1000 \times 5{\cdot}4521}{5{\cdot}3}$ c.cs. instead of 1000 c.cs.

Empty the contents of the crucible into a 200 c.c. beaker and wash out the crucible with several small washes of hot water. Add more hot water till the volume of solution is about 100 c.cs. Stir carefully with a light glass rod till the salt is completely dissolved. Allow the solution to cool. Make up to 1000 c.cs. by transferring to the litre flask and washing out the beaker with distilled water. Further water is added till, at a temperature of about 16° C., the solution reaches the mark. If the adjustment of Na_2CO_3 to 5·3 gms. was not made, add the additional amount of distilled water from the burette.

If correctly made up from pure Na_2CO_3, 1 c.c. of this solution should contain $\frac{5{\cdot}3}{1000}$ = ·0053 gm. Na_2CO_3, which is equivalent to ·00365 gm. HCl.

Checking the Standard Solution.—In order that the student may ascertain the true value of this solution he must check it; it may be correct or it may not. When once carefully checked this solution will serve for the preparation of standard acids or other standard alkalies. On the accuracy of this one standard depends the accuracy of all results.

Hydrochloric acid, the substance to be analysed, may also be used to check the solution as follows:—Fill the 50 c.c. burette with $\frac{E.}{5}$ HCl, prepared approximately from the reagent bottle. Into each of four narrow 200 c.c. beakers measure very carefully 20 c.cs. $\frac{E.}{5}$ HCl. Cover and set aside two of these portions.

Fill a clean burette with $\frac{N.}{10}$ Na_2CO_3. To the contents of each of the two beakers add 2 drops methyl orange solution, adjust the solution in the burette to zero, and under it, on a small square of white paper, place one of the beakers and contents. Proceed to titrate the solution by slowly adding the solution from the burette a little at a time, stirring with a light glass rod between each addition. About 36 c.cs. may thus be run in, but after this the additions must be made more cautiously, till finally the solution is added drop by drop till the pink colour just disappears. Note the number of c.cs. used. Repeat the operation with the second portion. The duplicates should not differ by more than ·1 c.c. provided the burette from which the $\frac{E.}{5}$ HCl was measured has been calibrated, and any corrections necessary made. The same remark applies to the burette used for the titration.

If the duplicates do not agree closely, weigh out another 20 c.cs. $\frac{E.}{5}$ HCl and repeat the operation. If this result does not agree with one of the first two, either the burettes are badly calibrated or the student's work is bad, or

perhaps both. It is of course assumed that the temperatures of the two solutions are approximately equal.

Proceed now to estimate the chlorine in the two reserved samples by means of the Gravimetric method previously given, taking care that any considerable excess of $AgNO_3$ is avoided. The duplicates should agree closely.

As a concrete example assume the following results:—

Average of titrations = 40·1 c.cs.

Average Cl in 20 c.cs. $\frac{E.}{5}$ HCl = ·1432 gm. = ·1472 gm. HCl.

But 1 c.c. $\frac{N.}{10}$ Na_2CO_3 should be equivalent to ·00365 gm. HCl.

Therefore ·1472 gm. HCl should require $\frac{·1472}{·00365}$ = 40·33 c.c. $\frac{N.}{10}$ Na_2CO_3.

That is, the $\frac{N.}{10}$ Na_2CO_3 solution is slightly strong, 40·1 c.cs. having the neutralising power of 40·33 c.cs. of the desired solution. The bulk of the solution must now be diluted in the proportion of 40·1 to 40·33. Transfer the alkaline solution to a measuring cylinder. Note its volume; for example, 880 c.cs. Now

401 : 403 : : 880 : 884·4

Add therefore to the alkali solution 4·4 c.cs. distilled water from a burette.

The student now has checked the accuracy of and adjusted the strength of the standard solution to $\frac{N.}{10}$ Na_2CO_3. It may appear to him at this stage that volumetric analysis can hardly lay claim to speed. He must remember, however, that from this one standard solution, solutions sufficient for hundreds of analysis may quickly and accurately be prepared. In practice it is usual to prepare instead of $\frac{N.}{10}$ solutions a stock of N. alkali and N. acid; but as the student has only a few analyses to perform, $\frac{N.}{10}$ solutions will serve.

The actual Analysis.—The student may now proceed to find the strength of any of the common mineral acids. A bottle is, for example, labelled E. HCl. The student is asked to determine the accuracy of the label value.

Knowing the approximate strength of the acid, the student will see that a 5 c.c. sample will require approximately 50 c.cs. $\frac{N.}{10}$ Na_2CO_3. As the error in measuring such a sample may be large in proportion to the volume measured, this error may be relatively lessened by measuring out 25 c.cs. into a 250 c.c. flask, and making up the bulk with distilled water to 250 c.cs. After shaking, remove 25 c.cs. with the pipette. This sample represents $\frac{1}{10}$th of the total, that is, 2·5 c.cs.

To this sample add 2 drops of methyl orange and titrate with the $\frac{N.}{10}$ Na_2CO_3. Repeat the titration on a fresh 25 c.cs. from the flask. Proceed till the results closely agree.

Now take another 25 c.cs. of the E. HCl; make up as before to 250 c.cs. and repeat the titrations. The results should agree with the former set.

Calculation.—As an example, assume that the average of the readings is 26·2 c.cs. $\frac{N.}{10}$ Na_2CO_3. Then 2·5 c.cs. E. HCl are neutralised by 26·2 c.cs. $\frac{N.}{10}$ Na_2CO_3. If accurately made up, they would be neutralised by 25 c.cs. $\frac{N.}{10}$ Na_2CO_3. That is, the strength of the acid analysed is $\frac{26·2}{25·0}$ E., or 1·048 E.

Or in percentages, 1 c.c. $\frac{N.}{10}$ $Na_2CO_3 = ·00365$ gm. HCl.

26·2 c.cs. $\frac{N}{10}$ $Na_2CO_3 = 26·2 \times ·00365$ gm. HCl $= ·09563$ gm. HCl.

If 2·5 c.cs. dilute HCl contain ·09563 gm. HCl, then 100 c.cs. of the dilute acid contain $\frac{·09563 \times 100}{2·5} = 3·8252$ gms. HCl. That is, the solution contains 3·8252% HCl.

(*b*) DETERMINATION OF THE STRENGTH OF A SOLUTION OF AMMONIA.

Apparatus, Reagents.—The usual volumetric and gravimetric apparatus. For analysis the student may take the bench reagent labelled 5E. NH_4HO. For the standard acid pure H_2SO_4 of specific gravity 1·840 or thereabouts is most suitable. Pure Na_2CO_3 (prepared as before) is necessary for standardising the acid.

Method, Reactions.—A certain volume of the ammonia solution is taken at a temperature of 16° C. (approximately). After adding the indicator, the solution is titrated with a standard solution of H_2SO_4.

$$2NH_4HO + H_2SO_4 = (NH_4)_2SO_4 + 2H_2O$$

The value and volume of the H_2SO_4 being known, the strength of the ammonia solution is easily calculated.

Preparation of the Standard Solution.—A normal solution of H_2SO_4 contains $\frac{2+32+64}{2} = 49$ gms. H_2SO_4 per litre. For present purposes the student may prepare a $\frac{N.}{10}$ solution as follows:—

Measure out 3 c.cs. H_2SO_4 (S.G. 1·84). This quantity weighs about 5·5 gms. To this add about 100 c.cs. distilled water, and when cool transfer to the test-mixer and make up to 1000 c.cs. at about 16° C.

Checking and adjusting the Standard.—Measure out from the burette 4 samples of 20 c.cs. each. Fill a burette with $\frac{N.}{10}$ Na_2CO_3. Add to each of the first two samples two drops of methyl orange and titrate with the $\frac{N.}{10}$ Na_2CO_3. Note the readings. Dilute each of the other two samples (as an additional check) to 100 c.cs. with distilled water, and in each of them estimate the SO_3 by precipitation with $BaCl_2$ (see Gravimetric Analysis), using preferably a Gooch crucible for filtration.

As an example, assume that the following results are obtained.

Average of titrations, 22·4 c.cs. $\frac{N.}{10}$ Na_2CO_3.

SO_3 found ·8953 gm. = 1·097 gm. H_2SO_4.

Now 1 c.c. $\frac{N.}{10}$ Na_2CO_3 = ·0049 gm. H_2SO_4; therefore

22·4 „ „ „ = 1·0976 gms. H_2SO_4, which agrees closely with the check by precipitation.

But 20 c.cs. $\frac{N.}{10}$ H_2SO_4 should contain $20 \times ·0049 = 0·98$ gm. H_2SO_4; that is, the acid is too strong in the proportion of 1·097 : ·980. In practice, the chemist adopts one of two courses:—

1. A factor is calculated, and is then used in all subsequent determinations.
2. The acid is adjusted by the addition of water and rechecking.

Both methods give equally accurate results; the first method, being much more rapid, is better suited to the busy chemist. The factor is calculated thus: If the acid were exactly $\frac{N.}{10}$, 20 c.cs. would require 20 c.cs. $\frac{N.}{10}$ Na_2CO_3 for neutralisation; but 22·4 c.cs. were required, therefore $\frac{22·4}{20} = 1·12$ is the required factor, and all readings of titrations with this acid must be multiplied by this factor.

If the second course is adopted the strength is adjusted as follows: Every 20 cc.s. of the acid must be diluted to 22·4 c.cs. Measure the volume of acid and dilute in this proportion. Titrate as before with $\frac{N.}{10}$ Na_2CO_3 and readjust if not quite accurate. The student will find this process rather troublesome, more especially if he over-dilutes the solution of acid. If in the least doubt, he should keep the acid a little on the strong side, as it is much easier to add water than acid.

Having standardised the acid by either of these methods, the student may proceed to the actual analysis.

Details of the Analysis.—From the reagent bottle, at a temperature of about 16° C., carefully measure by the burette 20 c.cs. of the 5 E. NH_4HO. Dilute with distilled water to 500 c.cs. After thorough mixing, measure out two portions of 20 c.cs. each and to each portion add about 1 c.c. neutral litmus solution.

Titrate each portion with the $\frac{N.}{10}$ H_2SO_4 till neutral, as shown by the indicator. The duplicates, as usual, should agree. Repeat the operation (as a check on the sampling) with a fresh sample from the reagent bottle.

Calculations.—Assume, for example, that the average reading is 38·8 c.cs. $\frac{N.}{10}$ H_2SO_4. The volume of 5E. NH_4HO corresponding to this is $20 \times \frac{20}{500} =$ ·8 c.c. If correctly made up, ·8 c.c. 5E. NH_4HO should require $·8 \times 5 \times 10 = 40$ c.cs. $\frac{N.}{10}$ H_2SO_4. Therefore the real strength of the ammonia is $\frac{38·8}{40}$ 5 E. or $·97 \times 5E. = 4·85$ E. Supposing the student is using the unadjusted standard solution and factor, the figures will be somewhat as follows:—

Average reading will be 34·6 c.cs. H_2SO_4 ($\frac{N.}{10}$ unadjusted), multiplying by the factor $34{\cdot}6 \times 1{\cdot}12 = 38{\cdot}752$, or to the nearest decimal in the first place, 38·8 c.cs. $\frac{N.}{10}$ H_2SO_4. The remainder of the calculation is the same as the preceding. The student must remember that the factor 1·12 was assumed merely as an example, and that this factor, if used, must be accurately determined.

(*c*) THE ESTIMATION OF CHLORINE IN $BaCl_2,2H_2O$ VOLUMETRICALLY BY STANDARD ALKALI AND ACID.

Apparatus and Reagents.—The usual volumetric outfit. For practice, the student may procure some pure barium chloride. The standard $\frac{N.}{10}$ Na_2CO_3 and $\frac{N.}{10}$ H_2SO_4 are again made use of.

Method, Reactions.—To the $BaCl_2$ solution $\frac{N.}{10}$ Na_2CO_3 is added from the burette till decidedly alkaline.

$$BaCl_2 + Na_2CO_3 + xNa_2CO_3 = \underline{BaCO_3} + NaCl + xNa_2CO_3$$

The total volume of alkali added is noted. Then, when the precipitate has settled, a known volume of the clear liquid is taken and the excess of alkali (xNa_2CO_3) is titrated with $\frac{N.}{10}$ H_2SO_4. From the figures thus obtained the amount of alkali that combined with the acid of the barium chloride is obtained, and from this the percentage of chlorine present.

Details of the Analysis.—Weigh out two portions of about ·3 gm. of the pure dry salt. Transfer to 200 c.c. beakers, and dissolve each portion in 150 c.cs. distilled water. When dissolved, add from a burette $\frac{N.}{10}$ Na_2CO_3 till decidedly alkaline to litmus paper (about 35 c.cs. should be sufficient for ·3 gm. of the salt). Transfer the liquid and precipitate to the 250 c.c. flask, washing out the beaker and bringing the solution up to the mark.

When the precipitate has settled, remove by the 50 c.c. pipette 50 c.cs. of the clear solution.

Titrate this as usual with $\frac{N.}{10}$ H_2SO_4. Remove another 50 c.cs. and repeat the titration. Submit the second ·3 gm. portion to the same treatment.

Calculation of Results. — Assume as an example that ·3 gm. of the salt are taken and that 35·1 c.cs. $\frac{N.}{10}$ Na_2CO_3 were added, and that 2·1 c.cs. of $\frac{N.}{10}$ H_2SO_4 were required in the titration of 50 c.cs. of the clear solution.

Then $5 \times 2{\cdot}1 = 10{\cdot}5$ c.cs. $\frac{N.}{10}$ H_2SO_4 are required to neutralise the excess of alkali.

Therefore the amount of alkali required to combine with the acid of the salt is $35{\cdot}1 - 10{\cdot}5 = 24{\cdot}6$ c.cs. $\frac{N.}{10}$ Na_2CO_3.

Now 1 c.c. $\frac{N.}{10}$ Na_2CO_3 = ·0035 gm. Cl, therefore

24·6 „ „ „ = ·0861 gm. Cl.

The percentage of chlorine = $\frac{·0861 \times 100}{·3}$ = 28·7%.

The theoretical percentage of chlorine in pure $BaCl_2 2H_2O$ is $\frac{71 \times 100}{244}$ = 29·1.

On looking through these calcuations, the student should notice that any error in the reading of the acid used in titration is magnified five times in the multiplication. Thus, if instead of 2·1 c.cs. the reading be 2 c.cs., the results work out as follows:

Percentage chlorine = $\frac{·8785 \times 100}{·3}$ = 29·28.

Great care is therefore necessary in reading the burette. The liability to error may be lessened by titrating two lots of 100 c.cs. each, or better still, one lot of 200 c.cs. of the clear liquid. Any error in reading thus suffers much less magnification by multiplication.

Note.—Store the remainder of the standard solutions in Winchester bottles.

CHAPTER VII.

ANALYSIS BY OXIDATION OR REDUCTION.

In this chapter the student is required to perform the following estimations, some of which will again be considered under "Mixed Analysis."

(*a*) The Estimation of Iron by Standard $K_2Mn_2O_8$ Solution.
(*b*) " " " Calcium " " "
(*c*) " " " Iron " $K_2Cr_2O_7$ "
(*d*) " " " Copper by I and Standard $Na_2S_2O_3$.
(*e*) " " " Chlorine in Bleaching Powder.

(*a*). THE ESTIMATION OF IRON BY STANDARD SOLUTION OF POTASSIUM PERMANGANATE (Marguerite's Method).

Apparatus, Reagents.—The usual volumetric apparatus. For standardising the solution soft iron wire such as is used for binding flowers is best suited. This wire contains 99·6% of iron. Pure $K_2Mn_2O_8$ is required for the standard solution. If in doubt concerning its purity it may be purified by crystallising twice from hot distilled water and drying at 100° C. For analysis, the student may take a sample of pure $FeSO_4,7H_2O$ or pure $FeSO_4,(NH_4)_2SO_4,6H_2O$ (ferrous ammonia sulphate), and a ferric salt such as $Fe_2(SO_4)_3$. The application of this and the Bichromate method to ores will be considered later under "Mixed Analysis."

Method, Reactions.—When $K_2Mn_2O_8$ is added to a solution of $FeSO_4$ the following reaction takes place in the presence of H_2SO_4.

$10FeSO_4 + K_2Mn_2O_8 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$,

or 316·2 parts by weight of $K_2Mn_2O_8$ will oxidise 560 parts by weight of Fe. The free H_2SO_4 is always necessary, as it prevents the formation of a brown precipitate of manganous oxide. If the free acid be HCl the solution to be titrated must be kept very dilute and at a low temperature, or chlorine may be liberated and spoil the analysis.

It should be noted that organic matter of any kind will decompose the permanganate, hence it is preferable to use burettes with glass cocks instead of the rubber fitting.

When titration with the permanganate is complete, a permanent pink colour results. Knowing the volume and value of the permanganate, the percentage of iron is easily calculated.

Preparation of the Standard Solution $\left(\frac{N.}{10}\right)$.—Carefully weigh out 3·156 gm. of the pure dry $K_2Mn_2O_8$. Transfer to the litre flask and add about 500 c.cs. distilled water, and when dissolved, make the solution up to the mark at about 16° C. Store in a glass stoppered bottle, and when not in use keep in the dark. This solution will keep for months, but it is advisable that the student should restandardise a solution when required again after

standing some time. The length of time will depend upon the nature of the solution; a few days in some cases, or a few weeks in others.

Checking the Standard Solution.—If carefully prepared from the pure salt as directed, the solution should be almost exactly $\frac{N.}{10}$; but the student, to be absolutely sure, must check the standard. Only one method is given here. For others he may consult Sutton or Blair*.

Thoroughly clean a piece of the iron wire about 25 cm. long by drawing it through a piece of fine sandpaper doubled between the fingers. Continue till perfectly bright, and then finish by drawing through a piece of clean dry linen rag. Avoid handling the cleaned wire with the fingers. Weigh out two pieces, each of about ·1 gm., using the assay balance if available. Note the exact weights of the two portions.

Take a 300 c.c. flask and clamp it at an angle on a retort stand. Fit it with a cork and delivery tube bent to lead down into a beaker. In the flask pour 100 c.cs. E. H_2SO_4 and in the beaker a solution of pure Na_2CO_3. To the solution in the flask add about half a gram of $Na_2CO_3,10H_2O$ (crystal). This fills the flask with CO_2. Quickly insert the iron wire, then the cork and tube, and set the beaker so that the tip of the tube is under the surface of the solution. Apply a low bunsen flame to the flask till the iron is all dissolved. Remove the flame, and, on cooling, the solution in the beaker rises and enters the flask and at once effervesces, forming CO_2 which drives the liquid down again. Remove the cork and tube. The flask now contains the solution and CO_2 (these precautions are taken to prevent the $FeSO_4$ being oxidised by the air to $Fe_2(SO_4)_3$. Quickly cool the flask under the tap. Cork it and fill the burette with $\frac{N.}{10}$ $K_2Mn_2O_8$. Place the flask underneath the burette; remove the cork and proceed to titrate with the permanganate, holding the flask by the neck with the left hand and manipulating the tap with the right. Agitate the contents of the flask by swirling after (or during) each addition, running the solution in rapidly so long as the colour is quickly destroyed, but when the colour becomes somewhat persistent proceed more slowly till the final adjustment is made by single drops. Note the number of c.cs. used, reading as far as possible to the second decimal place, and repeat the operation with the second piece of wire.

Assume, for example, that the two pieces of wire weigh ·1024 gm. and ·0984 gm., and that the volume of $\frac{N.}{10}$ $K_2Mn_2O_8$ required for each was 18·28 c.cs. and 17·50 c.cs. respectively. The actual amount of iron taken is $·1024 \times ·996 = ·1020$ gm. and $·0984 \times ·996 = ·0980$ gm.

If the solution is exactly $\frac{N.}{10}$ $K_2Mn_2O_8$, one c.c. should contain ·003156 gm. $K_2Mn_2O_8$, which is equivalent to ·0056 gm. Fe.

With the first portion 1 c.c. $K_2Mn_2O_8 = \frac{·1020}{18·28} = ·0056017$ gm. Fe.

„ second „ „ $= \frac{·0980}{17·50} = ·005600$ „

These results should not differ by more than ·00002 gm., and the standardisation must be proceeded with till such results are obtained.

Label the storage bottle $\frac{N.}{10}$ $K_2Mn_2O_8$. 1 c.c. = ·00560 gm. Fe

* *The Chemical Analysis of Iron.*

The Actual Analysis.

1. **The determination of Iron in Ferrous Ammonium Sulphate.**—Weigh out 1 gm. of the salt. Transfer to a 200 c.c. flask and dissolve in a little recently boiled distilled water. Add 100 c.cs. E. H_2SO_4. Titrate with $\frac{N.}{10}$ $K_2Mn_2O_8$. Note the volume used, and repeat the operation on a fresh portion of the salt.

Calculation.—Suppose 1·0124 gms. of the salt were taken and that 25·75 c.cs. $\frac{N.}{10}$ $K_2Mn_2O_8$ were required for titration.

$$25{\cdot}75 \text{ c.cs. } \frac{N.}{10} K_2Mn_2O_8 = {\cdot}0056 \times 25{\cdot}75 = {\cdot}1442 \text{ gm. Fe}$$

$$= \frac{{\cdot}1442 \times 100}{1{\cdot}0124} = 14{\cdot}24\%$$

Theoretically, 362 parts $FeSO_4,(NH_4)_2SO_4,6H_2O$ contain 56 parts Fe by weight, or 14·28%.

2. **The determination of Iron in Ferric Sulphate,** $Fe(SO_4)_3$.—Weigh out ·3 gm. of the white anhydrous sulphate and transfer it to a 200 c.c. flask. Dissolve the salt in a little distilled water. Make up to 100 c.cs. with distilled water and cautiously add 10 c.cs. 36E. H_2SO_4. Introduce about 5 gm. *pure* zinc; insert a cork with a long, thin, leading tube, the end of which dips into distilled water. The hydrogen thus evolved reduces the ferric to ferrous sulphate. Continue the action, aided by heat if necessary, till the Zn is completely dissolved. The ferric salt should now be completely reduced. Test by removing a drop on a glass rod and bringing it in contact with a drop of KCNS on a porcelain plate. If completely reduced no red tint should appear immediately on mixing the two drops.

If not quite reduced, add more zinc and a little acid if necessary. When thoroughly reduced and the zinc all dissolved, insert a cork after removing the delivery tube, and cork and cool rapidly under the tap.

Remove the cork and titrate as usual with the $\frac{N.}{10}$ $K_2Mn_2O_8$. Note the result. Repeat the operation on a fresh portion.

Calculation.—The necessary calculations are similar to those last given, and need not be repeated here. The student must, however, perform them as usual.

Note.—If the zinc used is not pure, a blank must be run to determine the amount of iron contained.

(*b*) THE ESTIMATION OF CALCIUM BY $\frac{N.}{10}$ $K_2Mn_2O_8$ SOLUTION.

Apparatus, Reagents.—The usual volumetric and gravimetric apparatus. The student may take for analysis pure precipitated $CaCO_3$. The $\frac{N.}{10}$ $K_2Mn_2O_8$ solution used for iron will serve again here.

Method, Reactions.—The calcium is precipitated as the oxalate, CaC_2O_4 according to the equation,

$$5CaC_2O_4 + 8H_2SO_4 + K_2Mn_2O_8 =$$
$$5CaSO_4 + 2MnSO_4 + K_2SO_4 + 2CO_2 + 8H_2O$$

That is, 315·6 parts $K_2Mn_2O_8$ oxidise $56 \times 5 = 280$ parts CaO, exactly half the quantity of Fe oxidised. Therefore 1 c.c. $\frac{N.}{10}$ $K_2Mn_2O_8 = ·0028$ gm. CaO. Knowing the volume and value of the $K_2Mn_2O_8$, the quantity of CaO is easily calculated.

Preparation and Checking of Standard Solution.—As the solution is already prepared and checked the student may proceed to the analysis.

The Actual Analysis.—Weigh out ·2 gm. of the pure carbonate of lime and transfer to a 200 c.c. beaker. Add 50 c.cs. distilled water and cover with a clock glass. Push the clock glass slightly aside and pour in a little at a time E. HCl. Continue adding the acid till the carbonate is all dissolved. Rinse the cover into the beaker by means of the wash bottle. Bring the bulk of the solution up to about 100 c.cs. Add 5E. NH_4HO till distinctly alkaline (check by smell). Heat to boiling and add hot $\frac{3E.}{5}$ $(NH_4)_2C_2O_4$ till in slight excess (about 10 c.cs. should do). Boil for a few minutes and allow to settle. Wash by decantation several times and finally bring the precipitate on to the filter. Wash the paper and precipitate with boiling water till no reaction is obtained for chlorine.

Under the beaker place a 200 c.c. flask. Push a hole through the bottom of the filter paper with a glass rod, and with a strong fine jet from the wash bottle wash through as much as possible of the precipitate. Wash the paper well with hot E. H_2SO_4, finishing with a few drops of E. HCl. Make up the contents of the flask to about 100 c.cs. Add 10 c.cs. 36E. H_2SO_4 and heat the contents of the flask to 70° C. and titrate rapidly with the $\frac{N.}{10}$ $K_2Mn_2O_8$. Note the result and run a duplicate as usual.

Calculations.—Assume that ·2124 gm. $CaCO_3$ were taken for analysis, and that 42·2 c.cs. of $\frac{N.}{10}$ $K_2Mn_2O_8$ were required for the titration.

The quantity of CaO present $= 42·2 \times ·0028 = ·11816$ gm. $= \frac{·11816 \times 100}{·2124}$ $= 55·91\%$.

Pure $CaCO_3$ should contain 56% CaO.

Further notes on this method will be given under "Mixed Analysis."

(*c*) THE ESTIMATION OF IRON BY STANDARD POTASSIUM BICHROMATE SOLUTION (Penny's Method).

Apparatus, Reagents.—For the preparation of the standard solution pure $K_2Cr_2O_7$ is required, also the iron wire as before, E. $SnCl_2$, $\frac{2}{5}$E. HCl and E. $K_6Fe_2C_{12}N_{12}$, freshly prepared and containing no ferrocyanide. A white porcelain plate is used for the indicator tests. For analysis the student may take another sample of the ferric sulphate previously used.

Method, Reactions.—If a solution of $K_2Cr_2O_7$ be added to a solution of a ferrous salt in presence of a strong free acid, oxidation takes place according to the equation,

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl = 3Fe_2Cl_6 + Cr_2Cl_6 + 2KCl + 7H_2O$$

The end point of this reaction is determined by an "external" indicator. A drop of the solution is brought in contact on a white porcelain plate with

a drop of $K_6Fe_2C_{12}N_{12}$ freshly prepared and containing no $K_4FeC_6N_6$. A rich blue results if the oxidation has not proceeded far. On adding to the solution more $K_2Cr_2O_7$ and testing a drop after each addition, the blue changes to a turbid greenish blue, to a grey, and finally to a brown. When the greenish blue has just disappeared the reaction is complete.

When estimating the iron in a ferric salt the reduction is generally brought about, not by zinc, but by stannous chloride, any slight excess of this salt being removed by a few drops of mercuric chloride.

Knowing the volume and value of $K_2Cr_2O_7$ solution used, the quantity of iron present is easily calculated.

Preparation of the Standard Solution $\frac{N.}{10}$ $K_2Cr_2O_7$.

As this salt yields 3 atoms of oxygen, which are equivalent to 6 atoms of hydrogen, the normal solution will contain $\frac{78+104{\cdot}8+112}{6} = 49{\cdot}13$ gms. per litre, therefore a $\frac{N.}{10}$ solution will contain 4·913 gms. per litre.

Weigh out this quantity of the salt; dissolve it in distilled water, and make up to 1 litre at 16° C. One c.c. of this solution should be equal to ·0056 gm. of iron.

Checking the Standard.—Weigh out two portions, each of about ·1 gm. clean soft iron wire. Place each portion in a 200 c.c. beaker. To each add 50 c.cs. 5E. HCl. Cover each beaker with a clock glass, and dissolve the wire with the aid of heat. When dissolved remove and rinse the covers. To the hot solution add drop by drop E. $SnCl_2$ with constant stirring. Continue till the yellow colour of the solution has completely disappeared, but avoid excess as far as possible. Dilute to 100 c.cs. Cool quickly and add drop by drop $\frac{2}{5}$E. $HgCl_2$. If no precipitate forms, insufficient $SnCl_2$ was added, and, on the other hand, too copious a precipitate will interfere with the titration. As soon as the precipitate, which should be white, has ceased forming, quickly fill the burette with the $\frac{N.}{10}$ $K_2Cr_2O_7$ and on a porcelain plate place with a glass rod about a dozen drops of uniform size of $K_6Fe_2C_{12}N_{12}$ solution. Proceed with the titration, constantly stirring, and removing now and then a drop of the solution on the rod, and bringing it in contact with a drop of the indicator on the porcelain plate. As soon as the bluish green has disappeared, read the burette.

Time will be saved by calculating in advance the probable quantity of solution required, and running in rapidly to within a few c.cs. of this quantity.

Assume that ·1022 gm. iron wire is taken and that it requires 18·2 c.cs. $\frac{N.}{10}$ $K_2Cr_2O_7$. Now ·1022 gm. of the wire contain ·1022 × ·996 = ·1018 gm. iron.

$$1 \text{ c.c. } \frac{N.}{10} K_2Cr_2O_7 = \frac{{\cdot}1018}{18{\cdot}2} = {\cdot}005594 \text{ gm. Fe}$$

Duplicates should agree within ·00002 gm. iron.

The Actual Analysis.—Weigh out ·3 gm. anhydrous $Fe_2(SO_4)_3$. Transfer to a 200 c.c. beaker. Treat exactly the same as when dissolving and reducing the iron wire, and titrate with the $\frac{N.}{10}$ $K_2Cr_2O_7$ as before.

Repeat the estimation on a fresh portion of the ferric sulphate.

Calculate the results as usual, and repeat the estimation if the duplicates do not agree. The results obtained by this method should agree with those obtained by the permanganate.

Note.—As HCl is a more common solvent than H_2SO_4, this method is preferable to the permanganate. The solution is more stable and is not affected by rubber, so that the cheaper form of burette may be used. It has the slight disadvantage that an external indicator is required, but with a little practice and careful observation the student will soon learn to sharply distinguish the 'end point.'

(*d*) THE VOLUMETRIC ESTIMATION OF COPPER BY IODINE AND STANDARD SODIUM THIOSULPHATE.

1. In $CuSO_4,5H_2O$.

Apparatus, Reagents.—For the preparation of the standard solution pure crystalline $Na_2S_2O_35H_2O$ and pure electrolytic copper are necessary, also a solution of starch in boiling water.

Method, Reactions.—When a solution of KI is added in excess to a solution of a cupric salt in either slightly acid or an acetic acid solution Cu_2I_2 is formed and I liberated thus,—

$$2CuSO_4 + 4KI = 2K_2SO_4 + Cu_2I_2 + I_2$$

This liberated iodine is now titrated with standard thiosulphate, using starch as an indicator,

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

As soon as this reaction is completed the dark blue colour given by the iodine and starch immediately disappears.

Knowing, then, that a certain weight of copper will liberate from excess of potassium iodide a certain weight of iodine, then, by measuring this quantity of iodine with a solution of thiosulphate of sodium, the volume and value of which are known, the quantity of copper present may be accurately calculated. Care must be taken to follow exactly the instructions given regarding the quantity of acid used, its expulsion and neutralisation.

Preparation of the Standard Solution.—A normal solution of $Na_2S_2O_3$, $5H_2O$ should contain $46+64+48+90=248$ gms. per litre and a $\frac{N.}{10}$ solution 24·8 gms. per litre.

Weigh out 24·8 gms. of the pure salt, which has been carefully powdered in a wedgewood mortar. Dissolve in a little distilled water and make up to 1 litre at 16° C.

If exactly $\frac{N.}{10}$, one c.c. of this solution is equivalent to ·0127 gm. iodine, which is equivalent to ·0063 gm. copper.

Standardising the Solution.—Weigh out two portions of clean copper foil each of about ·2 gms. and transfer to 200 c.c. flasks. To each add 5 c.cs. 16E. HNO_3. When the copper is dissolved boil down each lot to between one and two c.cs. Cool and add to each 5 c.cs. distilled water to dissolve the copper nitrate. Add to each 5 c.cs. 20 E. NH_4HO. The solution should now be strongly alkaline. Heat to boiling and boil for a few minutes to perfectly neutralise the acid in the nitrate of copper.

Remove and add to each 5 c.cs. 17 E. $HC_2H_3O_2$ and then 50 c.cs. of distilled water.

Fill the burette with the thiosulphate and titrate the brown solution till the brown colour becomes faint, and then add enough starch solution to produce a strong blue coloration. Titrate slowly till the blue colour vanishes, leaving a cream-coloured precipitate. This change takes place very suddenly, and at the first decided change the student should pause a few moments, as the colour generally completely disappears on standing a moment. Note the number of c.cs. used in each determination and calculate the value, in copper, of each c.c.

Duplicates should agree within ·00003 gm. of copper.

The Actual Analysis.—Weigh out about 1 gm. of the pure sulphate of copper. Transfer to a 200 c.c. beaker; dissolve in about 20 c.cs. distilled water; add 10 c.cs. 36E. H_2SO_4, and 30 c.cs. distilled water. In the solution place a strip of sheet aluminium about 7·5 cm. × 3·75 cm. × ·15 cm., turned up at right angles for about an inch at each end, the body of the strip resting flat on the bottom of the beaker. Cover the beaker and heat to boiling, and boil from five to seven minutes till the copper is all precipitated in the metallic form (test a little of the clear solution for copper). Now transfer the liquid into a 300 c.c. flask and as much of the copper as convenient, leaving the aluminium and a little adhering copper behind after rinsing well with the wash bottle. Set the beaker and aluminium aside. Let the copper in the flask settle and decant the liquid through a white filter paper. Wash the copper several times by decantation. Wash the paper once or twice, bringing any particles of copper down to the point. Place the beaker with the aluminium under the funnel. On the paper, drop by drop, add 4 c.cs. 16E. HNO_3 to dissolve any copper on the paper. When this has drained through, wash with three or four very small washes of hot water. When all the copper that may have been left in the beaker is dissolved, rinse the contents of the beaker into the flask, leaving the aluminium behind. Heat the flask and contents till all the copper is dissolved. Evaporate down to 1 to 2 c.cs., and proceed with the remainder of the analysis as in the standardisation of the thiosulphate by metallic copper. Repeat the operation on a duplicate sample.

Calculation.—Assume, for example, that 40 c.cs. $Na_2S_2O_3$ are required for 1·0012 gm. of the salt, and that 1 c.c. $Na_2S_2O_3$ equals ·00632 gm. copper. Then the quantity of copper present is $40 \times ·00632 = ·2528$ gm. The percentage is calculated as usual, and the results may be compared with those found by gravimetric methods. The standard solution may be relied on to keep for several weeks, but it is better for the student to make a point of re-checking a solution that has not been in use for some days.

2. The estimation of Copper in Ores by the Iodide method.—The standard solution is again used, and needs no further checking. The student may take for analysis a sample of copper pyrites, portion of which he may reserve (after reduction and sampling) for subsequent estimation by the Cyanide method.

The Analysis.—Powder the sample to pass an 80 sieve, and from this by quartering obtain a sample of a few grams. Grind this further in an agate mortar, and from this sample weigh out ·5 gm. The subsequent treatment as modified by A. H. Low (*Jour. Amer. Chem. Soc.*, xviii., No. 5, and contribution to Peters' *Copper*) is as follows:—

Transfer the ore to a 250 c.c. flask. Add 10 c.cs. 16E. HNO_3 and boil nearly to dryness. Add 10 c.cs. 16E. HCl and again boil. After 2 or 3 minutes add 10 c.cs. 36E. H_2SO_4 and heat strongly till white fumes rise

freely from the liquid. Cool. Add 40 c.cs. water and heat to boiling. Filter through a 7·5 cm. paper. Wash, and endeavour to keep the washings under 75 c.cs.

Proceed now with the aluminium precipitation as before described, except that in the case of ores Low strongly recommends the addition of about 1 gm. $KClO_3$ before evaporating down to between 1 and 2 c.cs. This oxidises any arsenic present to arsenic acid, which is inert. The titration is performed as usual. The student may later on check the results obtained here by means of the Cyanide method or the Electrolytic method. According to Low the Iodide method is equal in accuracy to the almost perfect Electrolytic method.

(*e*) THE DETERMINATION OF CHLORINE IN BLEACHING POWDER BY IODINE AND STANDARD HYPOSULPHITE.

Apparatus, Reagents, etc.—As before. The student may take for analysis a sample of ordinary commercial bleaching powder.

Method, Reactions.—If, to the milky liquid obtained by treating the powder with water, excess of KI be added, and then $HC_2H_3O_2$, the chlorine is liberated from the bleaching powder, which consists largely of $Ca(OCl)Cl$, and sets free an equivalent quantity of iodine.

$$Ca(OCl)Cl + 2HC_2H_3O_2 = Ca(C_2H_3O_2)_2 + H_2O + Cl_2$$
$$2KI + Cl_2 = 2KCl + I_2$$

This liberated iodine is then titrated with the hyposulphite, using starch as an indicator.

If the bleaching powder consisted wholly of $Ca(OCl)Cl$ it contains 55% of available chlorine—that is, chlorine which can be liberated by treatment with dilute acid; but the commercial variety generally contains other substances, and does not yield more than 36% available chlorine.

The Analysis.—Weigh out 5 gms. of the bleaching powder and transfer to a porcelain mortar. Rub up with about 50 c.cs. water till of the consistency of a thin cream. Allow to settle for a few minutes, and pour off the liquid into a litre flask. Repeat with another 50 c.cs. of water, and again with another lot, till the whole of the sample is transferred to the flask. Dilute to the mark with water.

Shake well, and remove with the pipette 50 c.cs. Add excess of KI; about 16 c.cs. of $\frac{E.}{5}$ KI will do. Render acid with 5E. $HC_2H_3O_2$. Titrate with the $\frac{N.}{10}$ $Na_2S_2O_3$, using the starch indicator as before.

Repeat the titration on another 50 c.cs. from the litre flask.

Calculation.—The $\frac{N.}{10}$ $Na_2S_2O_3$ solution has been standardised on pure copper. Assume it was found that 1 c.c. $\frac{N.}{10}$ $Na_2S_2O_3$ = ·00631 gm copper. Theoretically 1 c.c. $\frac{N.}{10}$ $Na_2S_2O_3$ = ·0127 gm. iodine = ·0063 gm. copper = ·00355 gm. chlorine.

Therefore ·1 c.c. of the $\frac{N.}{10}$ $Na_2S_2O_3$ = $\frac{·00355 \times 631}{630}$ = ·003555 grams chlorine.

The percentage of chlorine is then calculated as usual.

Concluding Note.—The analyses given in this chapter have been selected both on account of their utility to the technical chemist and on account of the variety of practice afforded the student in such work. It must be remembered that only a few of the most important methods have been described. The student who desires to follow the matter further should consult the authorities previously mentioned (Sutton and Schimpf), and for their special application to the work of the metallurgical chemist he may consult Furman's *Manual of Assaying* and Beringer's *Text Book*.

CHAPTER VIII.

ANALYSIS BY PRECIPITATION.

When we consider the ordinary gravimetric precipitations, it is evident that if the exact strength (as regards precipitation) of the precipitating reagent were known, and the exact end point of the precipitation were known, then we should be able to do away with the drying, incineration, and weighing, and perform the estimation volumetrically.

In certain cases this can conveniently be done, and in this chapter the following estimations will be considered :—

(*a*) **Chlorine by Precipitation with Silver Nitrate.**
(*b*) **Cyanogen by Precipitation with Silver Nitrate.**
(*c*) **Cyanogen by Precipitation with Mercuric Chloride.**
(*d*) **Lead by Precipitation with Ammonium Molybdate.**
(*e*) **Zinc by Precipitation with Potassium Ferrocyanide.**
(*f*) **Arsenic by Precipitation with Silver Nitrate and Titration with Ammonium Sulphocyanide.**
(*g*) **Manganese by Precipitation with Potassium Permanganate.**

Previously it has been the custom to estimate the various elements or compounds in substances of known composition—generally chemical compounds—thus affording an easy check on the accuracy of the work. Such checks, it is clear, cannot be obtained in the majority of metallurgical analyses, therefore in the following analyses ores and other substances coming within the scope of metallurgical chemistry will be taken for analysis in most cases, and the student's results must be checked by the demonstrator, who must demand the repetition of any analysis the results of which are unsatisfactory.

(*a*) THE VOLUMETRIC ESTIMATION OF CHLORINE BY PRECIPITATION WITH SILVER NITRATE.

Apparatus, Reagents.—Apparatus as usual. For the preparation of the standard solution, pure silver nitrate (preferably triple crystallized) is required. For practice in this analysis the student may first estimate the chlorine in pure sodium chloride, and then in a sample of river or well water.

Method, Reactions.—If a solution of $AgNO_3$ is added to a solution containing a chloride, a precipitate of $AgCl$ is formed so long as any chlorine remains uncombined with the silver. The end point may be determined (in the absence of acids) by adding a few drops of K_2CrO_4.

$$AgNO_3 + X,Cl = X,NO_3 + AgCl$$
$$\text{and } K_2CrO_4 + 2AgNO_3 = \underline{Ag_2CrO_4} + 2KNO_3$$

As soon as the silver has united with all the chlorine any excess of $AgNO_3$ forms a red precipitate with the K_2CrO_4.

Preparation of the Standard Solution.—As $AgNO_3$ is rather expensive, and as the quantity of solution required will not be great, the student need only prepare 500 c.cs. of the standard $\frac{N.}{10}$ $AgNO_3$.

N. $AgNO_3$ should contain 107·6 + 14 + 48 = 169·6 gms. $AgNO_3$ per litre; $\frac{N.}{10}$ $AgNO_3$ 16·96 gms. per litre.

Weigh out carefully 8·48 gms. pure $AgNO_3$, and transfer to the 500 c.c. flask. Add about 50 c.cs. distilled water, and when dissolved make up to the mark at 16° C.

1 c.c. of this solution should be equal to ·00355 gm. Cl.

Checking the Standard.—If the solution has been carefully prepared from pure $AgNO_3$ it hardly need be checked, but the student had better check the solution as follows :—

From the burette at about 16° C. measure out 25 c.cs. of the $\frac{N.}{10}$ $AgNO_3$ solution, and carefully precipitate and estimate gravimetrically the silver contained. 25 c.cs. should contain ·01076 × 25 = ·269 gm. Ag.

The Analysis.—1. Of Chlorine in Sodium Chloride.—Weigh out ·2 gm. sodium chloride (pure). Dissolve in a 200 c.c. beaker with about 50 c.cs. distilled water. Add three or four drops of E. K_2CrO_4.

Titrate with the $\frac{N.}{10}$ $AgNO_3$ from the burette until the red precipitate of chromate of silver, which is at first decomposed by the excess of silver, is just permanent.

Note the number of c.cs. used, and repeat the estimation on a fresh sample, and calculate the percentage of chlorine in the usual manner.

Note.—This titration must be performed on a cold neutral solution, as Ag_2CrO_4 is soluble in acids. This method reversed may be used for the estimation of silver. A modified method will be found in Furman, p. 240.

2. **The Analysis of Chlorine in River or Well Water.**—From an average sample of the water measure out 100 c.cs. into a 200 c.c. beaker. Add a few drops E. K_2CrO_4 and titrate as usual. Calculate the percentage of chlorine as usual, or estimate it as so many grains per gallon (see Water Analysis, Part III.).

If very little chlorine be present in the water it is better to take, say, 700 c.cs. and evaporate down to 100 c.cs. before titration. If 700 c.cs. be taken, then the centigrams of chlorine found give the number of grains per gallon; if 70 c.cs., the milligrams chlorine represent grains per gallon.

(*b*) THE VOLUMETRIC ESTIMATION OF CYANOGEN BY SILVER NITRATE.

Apparatus, Reagents, etc.—The same as in the last analysis, except that the chromate is not required. For analysis the student may take a solution prepared by the demonstrator, or a sample of 'gold' cyanide (KCN), which, if the potassium salt, will contain from 95% to 98% KCN. This salt now frequently contains NaCN, so that if estimating in percentages of KCN the results in these terms will run above 100%.

Method, Reactions.—If to a solution of KCN a solution of $AgNO_3$ be added the following reaction takes place,

$$KCN + AgNO_3 = AgCN + KNO_3$$

but this AgCN is soluble in KCN, forming the soluble double cyanide KCN,AgCN, and as long as there remains in the solution some KCN not converted into this double salt no permanent precipitate forms, but immediately the last trace of KCN is absorbed to form the double salt then the slightest excess of $AgNO_3$ will produce a permanent precipitate.

$$2KCN + AgNO_3 = KCN,AgCN + KNO_3$$

It is evident, then, that if the strength of the $AgNO_3$ solution is known the quantity of CN present may readily be estimated, and, as is frequently required, calculated to KCN. In technical work, where the presence of ferrocyanides and other salts may obscure the end point, the addition of a few c.cs. N. NaHO and a few drops of E. KI is advisable, and even then, unless precautions be taken (see Sutton, pp. 218–226), the end point may still be indistinct, but with the materials mentioned for practice the student should have no difficulty, especially if he use an alkali and KI, in obtaining a distinct end point marked by a permanent opalescence.

The Standard Solution.—The balance of the $\frac{N.}{10}$ $AgNO_3$ used in the last estimation will serve again here.

$$1 \text{ c.c. } \frac{N.}{10} AgNO_3 = \cdot0052 \text{ gm. } CN = \cdot013 \text{ gm. } KCN$$

as by the second equation one molecule of $AgNO_3$ is required for every two molecules of KCN to form the soluble double cyanide KCN,AgCN. In routine work 'empirical' solutions are generally used. For example, in the United States 6·535 gms. $AgNO_3$ to the litre forms the standard solution. Then 10 c.cs. KCN solution are taken for the estimation, and each c.c. of $AgNO_3$ solution used represents 1 lb. of KCN in the ton (2000 lbs.) of solution.

Or again, as is the practice in the British Colonies, the standard solution contains 17 gms. $AgNO_3$ per litre. Then 13 c.cs. of the cyanide solution to be tested are taken, and the number of c.cs. of $AgNO_3$ used divided by ten gives the percentage of KCN in the solution.

The strength of the solution has already been checked by precipitation.

The Analysis.—Weigh out quickly about 10 gms. of the roughly powdered cyanide and transfer to the 1000 c.c. test-mixer. Add about 250 c.c. distilled water. Stopper and shake. When dissolved make up to 1000 c.cs. With the pipette transfer 50 c.cs. into a 200 c.c. Erlenmeyer flask. Add a few drops E. KI, and titrate with the $\frac{N.}{10}$ $AgNO_3$, running in a little, and then rapidly swirling the contents of the flask. After a number of additions and agitation by swirling, the precipitate formed hangs much longer before dissolving. The solution is then run in drop by drop with agitation till a faint yet permanent opaline or milky tint is formed. This is best judged by placing a small square of black paper under the flask.

Note the number of c.cs. used, and repeat the estimation on another 50 c.cs. of the solution.

Calculation of Results.—Assume that 38·2 c.cs. $AgNO_3$ are required for 50 c.cs. KCN solution, 38·2 c.cs. $\frac{N.}{10}$ $AgNO_3 = ·013 \times 38·2 = ·4966$ gms. KCN. But 50 c.cs. contain ·5 gm. of the salt, therefore 100 c.cs. will contain 1 gm. of the salt, of which $·4966 \times 2 = ·9932$ gms. are potassium cyanide, or in other words the salt contains 99·32% KCN (assuming no NaCN to be present).

Note on Testing Solutions containing KCN.—The student may test a solution if dilute (say below 5%) by measuring out 50 c.cs. and titrating as before. If a strong solution is to be tested it should be diluted to a given volume, and 50 c.cs. of the diluted solution taken and the results multiplied according to the degree of dilution. The methods used in technical work have been indicated above, and the student may adopt them when he returns to this work in Laboratory Ore Tests, Part III.

(*c*) THE VOLUMETRIC ESTIMATION OF CYANOGEN BY MERCURIC CHLORIDE.

Apparatus, Reagents.—Apparatus as before. For the standard solution, pure $HgCl_2$ is required. For analysis the student may take further portions of the materials used in the last estimation.

Method, Reactions.—If to an ammoniacal solution of KCN a solution of $HgCl_2$ be slowly added, $Hg(CN)_2$ is formed and is soluble in water. When this reaction is complete any further addition of $HgCl_2$ results in the formation of a white precipitate,

$$HgCl_2 + 2KCN = Hg(CN)_2 + 2KCl$$
$$HgCl_2 + 2NH_4HO = \underline{NH_2HgCl} + NH_4Cl + 2H_2O$$

Knowing the strength and volume of the $HgCl_2$ solution used, the quantity of CN or KCN may be calculated.

Standard Solution.—An $\frac{N.}{10}$ $HgCl_2$ will contain $\frac{270·54}{10} = 27·054$ gms. of the salt per litre, and according to the equation 1 c.c. is equivalent to ·0052 gm. CN or ·013 gm. KCN.

It will be sufficient if the student prepare 250 c.cs. of this solution. Therefore dissolve 6·7635 gms. of the salt in distilled water and make up to 250 c.cs.

The student need not at present check the accuracy of this standard, but may compare the results obtained with those from the Silver Nitrate method.

The Analysis.—Proceed exactly as in the Silver Nitrate method, weighing or measuring the same quantities of material operated on, and titrating after adding excess of NH_4HO(no KI) till a faint but permanent opalescence is obtained.

Run duplicates, calculate the percentage of KCN, and compare the results with those previously obtained. With pure salts this method is very accurate, but with impure salts it is not so reliable as the previous method.

Note.—When instructed to estimate the percentage of KCN present, it is assumed that all the CN radical is united to K. This may or may not be so, but in Cyanide work it has become the custom to speak of the strength of a solution in percentage of KCN.

(*d*) THE VOLUMETRIC ESTIMATION OF LEAD BY AMMONIUM MOLYBDATE. Alexander's Method.

Apparatus, Reagents.—The usual apparatus. For the standard solution, ammonium molybdate is required [$(NH_4)_2MoO_4$], or by a simple calculation the heptamolybdate $(NH_4)_6Mo_7O_{24},4H_2O$ which is non-deliquescent, or the trioxide MoO_3 dissolved in NH_4HO may be used. For an indicator a solution of 1 gm. tannin in 500 c.cs. water is used. For analysis the student may take a siliceous galena ore, containing roughly about 50% galena and 50% quartz.

Method, Reactions.—When $(NH_4)_2MoO_4$ is added to a hot solution of $Pb(C_2H_3O_2)_2$ the following reaction takes place,

$$Pb(C_2H_3O_2)_2 + (NH_4)_2MoO_4 = \underline{PbMoO_4} + 2NH_4C_2H_3O_2$$

To determine the end point of this precipitation, an external indicator, 'tannin,' is used; a drop on a white porcelain plate giving a yellow colour with any excess of the molybdate of ammonia. Knowing the strength and volume of the standard solution used, the quantity of lead is easily calculated. The ore is broken up with HNO_3 and H_2SO_4, and the lead obtained as the sulphate, which is dissolved in hot $NH_4C_2H_3O_2$.

Preparation of the Standard Solution.—An $\frac{N.}{20}$ solution will be found most convenient. Dissolve 9·8 gms. $(NH_4)_2MoO_4$ (or equivalents of $(NH_4)_6Mo_7O_{24},4H_2O$ or MoO_3 in NH_4HO) in distilled water and make up to one litre at 16° C. If the solution is not clear a few drops of strong ammonia will generally clarify it.

$$1 \text{ c.c. } \frac{N.}{20} (NH_4)_2MoO_4 = \text{about } \cdot 01 \text{ gm. lead}$$

Checking the Standard.—Weigh out two portions, each of ·2 gm. pure lead sulphate. Transfer to 300 c.c. beakers. Dissolve in a little hot 5E. $NH_4C_2H_3O_2$, adding a little at a time, and heating till solution is complete. Acidify with acetic acid. Dilute each lot to 200 c.cs. with hot water. Titrate with the molybdate solution, testing a drop every now and then with a drop of the tannin solution on a porcelain plate. Immediately the molybdate is in excess a yellow colour is obtained. Note the number of c.cs. used.

Assume that 13·62 c.cs. are required for ·2016 gm. $PbSO_4$. But ·2016 gms. $PbSO_4$ contain $\frac{\cdot 2016 \times 207}{303} = \cdot 1377$ gm. Pb.

$$\text{Therefore 1 c.c. } \frac{N.}{20} (NH_4)_2MoO_4 = \frac{\cdot 1377}{13 \cdot 62} = \cdot 01011 \text{ gm. Pb.}$$

Duplicates should agree within ·00005 gm. Pb.

The Analysis.—Weigh out ·5 gm. of the sampled and finely powdered galena. Transfer to a casserole or a porcelain dish with an inverted funnel placed inside. Cautiously add 15 c.cs. 16E. HNO_3 and 10 c.cs. 36E. H_2SO_4. Heat just to boiling, and continue at this temperature till white fumes of SO_3 appear. The excess of HNO_3 is then expelled. Remove from the heat and wash down the lid or cover when cool. Add 50 c.cs. cold distilled water. Stir well with a glass rod, breaking up any residue. Gently boil to dissolve all soluble sulphates.

Let settle, and pour off most of the liquid through a filter paper. Wash by decantation twice with hot E. H_2SO_4 and once with hot water. To the white residue in the beaker add a little hot $NH_4C_2H_3O_2$ and heat a few minutes. Decant through the filter, having placed a clean 300 c.c. beaker under the funnel. Repeat the treatment till the $PbSO_4$ is all dissolved. Test by removing a drop of the solution from the beaker and bringing it into contact with a drop of NH_4HS on a porcelain plate. Wash out the beaker with hot water and wash the filter till the lead is all through.

Acidify the filtrate with acetic acid and dilute to 200 c.cs. Titrate as before with the $\frac{N.}{20}$ $(NH_4)_2MoO_4$. Note the number of c.cs. used and calculate the percentage of lead.

Repeat the estimation on another sample of the ore. The duplicate should agree within ·1%.

Note.—This method (see the *Engineering and Mining Journal*, vol. lv., No. 13, 1893) is well suited for the estimation of lead in ores and mattes, being both accurate and quick. With some practice a complete estimation can be made in about half an hour.

(*e*) THE VOLUMETRIC ESTIMATION OF ZINC BY POTASSIUM FERROCYANIDE. (Fahlberg's Method, as modified by von Schulz and Low).

Apparatus, Reagents.—The usual apparatus. For the preparation of the standard solution pure $K_4FeC_6N_6$ (free from $K_6Fe_2C_{12}N_{12}$) is used, and pure ZnO is employed for checking the standard. As an indicator a solution of uranium acetate is employed. In the preparation of the ore for analysis the following solutions are required :—About 100 c.cs. of a solution of $KClO_3$ crystals in strong HNO_3, prepared by shaking the crystals and acid in a flask. Solid NH_4Cl and 20E. NH_4HO are also required, and a litre of $\frac{E.}{5}$ NH_4Cl. If copper is present, a number of small strips of thin sheet aluminium are required for its precipitation.

For analysis, the student may take a zinc ore containing a fair percentage of zinc blende (ZnS).

For fuller details regarding the technical application of this and other volumetric methods the student is referred to Furman's *Manual of Assaying.*

Method, Reactions.—If to a hydrochloric acid solution of a zinc ore, free or freed from elements such as copper, iron, manganese, etc., a solution of potassium ferrocyanide be added, the zinc is precipitated as zinc ferrocyanide.

$$2ZnCl_2 + K_4FeC_6N_6 = \underline{Zn_2FeC_6N_6} + 4KCl$$

The end point of this reaction is determined by testing on a porcelain plate a drop of the solution with a drop of uranium acetate solution. As long as there is not an excess of $K_4FeC_6N_6$ the drop of uranium acetate remains yellow, but as soon as the ferrocyanide is in excess it turns a light brown. Before the solution of the ore is ready for titration iron and copper must be removed, if present, as they interfere with the reaction.

Preparation of the Standard Solution. — Dissolve 42·2 gms. pure $K_4FeC_6N_6,3H_2O$ in water and make up to 1 litre at 16° C.

Checking the Standard.—Weigh out in duplicate ·2 gm. pure ZnO, recently ignited to free it from any carbonate. Dissolve in 5 c.cs. 10E. HCl, and add 50 c.cs. water, using a 300 c.c. beaker. Add 20E. NH_4HO in slight

excess, and neutralise with HCl, using litmus paper as an indicator, a small piece of the paper being floated in the liquid. Add an excess of 10 c.cs. 10E. HCl and dilute with distilled water to 250 c.cs. The solution is now titrated with the ferrocyanide from a burette, the solution being run in rapidly, at first a few c.cs. at a time, until nearing the finishing point. A drop is tested, after each addition, by a drop of uranium acetate on the porcelain slab. Finish carefully, and as soon as the drop of uranium solution turns brown read the burette.

Treat the duplicate in the same way, and calculate the value of one c.c. of the ferrocyanide solution.

The neutralisation and addition of acid are for the purpose of having the conditions of the solution on standardisation similar to those in the actual analysis.

The Analysis.—Weigh out ·5 gm. of the sampled and finely powdered ore. Transfer to a porcelain dish or casserole. Add 15 c.cs. aqua regia. Cover, and when dissolved rinse the cover and evaporate to dryness. If particles of the ore remain undecomposed add gradually 15 c.cs. of the $KClO_3$,HNO_3 solution. Cover, and warm gently until greenish fumes cease to be given off. Then boil just to dryness on the hot plate. Cool. Add 7 gms. solid NH_4Cl, 15 c.cs. 20E. NH_4HO, and 25 c.cs. hot water. Boil for a minute, stirring with a rod to break up any lumps or clots. Filter into a 250 c.c. flask and wash several times with hot $\frac{E.}{5}$ NH_4Cl.

If a considerable precipitate has been formed it should be gently scraped off the paper with the assistance of the wash bottle and transferred to a porcelain dish, the excess of water evaporated and 15 c.cs. HNO_3,$KClO_3$. Treat as before with the NH_4HO,NH_4Cl and water. Filter and combine the first and second filtrates.

This treatment of the first precipitate is for the purpose of removing any traces of zinc hydrate that may have been precipitated with the iron.

If the combined filtrate is blue in colour, copper is present and must be removed as follows:—Neutralise with HCl and then add 10 c.cs. 10E. HCl. Heat to about 70° C. Now add a number of the aluminium strips. Shake till the copper is all precipitated.

If, however, the copper is absent, neutralise the combined filtrates with HCl, add then 10 c.cs. 10E. HCl, and the solution, if cool, is ready for titrating.

Titrate as before, and note the volume used. Repeat the determination on a fresh sample of the ore. Duplicates should agree within ·2%. Report the results in percentage of zinc.

Note.—The student should note the importance, when dealing with complex ores, of standardising the solution under similar conditions to those existing in the solution to be analysed.

(*f*) THE VOLUMETRIC ESTIMATION OF ARSENIC (Pearce's Method).

Apparatus, Reagents.—The usual apparatus. For precipitation E. $AgNO_3$ may be used. For the standard solution NH_4CNS is used, and as an indicator a saturated solution of iron alum. For the solution of the silver arseniate, pure HNO_3 is required.

Method, Reactions.—The ore containing the arsenic is fused with a mixture of KNO_3 and Na_2CO_3, the arsenic being thus oxidised to sodium

arseniate and potassium arseniate. On dissolving this arseniate and carefully neutralising the solution and adding neutral $AgNO_3$ in slight excess a brick red precipitate of Ag_3AsO_4 is obtained,—

$$Na_2HAsO_4 + 3AgNO_3 = Ag_3AsO_4 + 2NaNO_3 + HNO_3$$
$$or\ NaH_2AsO_4 + 3AgNO_3 = Ag_3AsO_4 + NaNO_3 + 2HNO_3$$

To be complete, this precipitation must take place in a neutral solution; and as some HNO_3 is liberated by the reactions, a second neutralisation is necessary if the amount of arsenic is large.

The solution of Ag_3AsO_4 is dissolved in HNO_3, a little iron alum added, and a standard solution of NH_4CNS run in till by excess a brownish red is obtained.

$$NH_4CNS + AgNO_3 = NH_4NO_3 + \underline{AgCNS}$$

From the silver found and the formula Ag_3AsO_4 the quantity of arsenic is calculated. As a large amount of Ag_3AsO_4 is formed from a small amount of As, the sample for analysis may be taken as ·5 gm. ore when poor in arsenic and ·2 gm. ore when rich in arsenic. Arsenical pyrites may be taken for analysis.

Preparation of the Standard Solution.—As the salt is deliquescent it cannot be weighed very accurately, therefore weigh out roughly about 8 gms. NH_4CNS. Dissolve in distilled water and make up to 1 litre at about 16° C. Roughly this is an $\frac{N.}{10}$ solution.

Checking the Standard.—Weigh out in duplicate about ·2 gm. test silver (see Assaying). Dissolve in a flask in a small quantity of pure 5E. HNO_3. When dissolved make up to about 150 c.cs. Add 5 c.cs. of the iron-alum solution and titrate with the $\frac{N.}{10}$ NH_4CNS till the brown ferric thiocyanate just appears.

Calculate the value of 1 c.c. in terms of silver, and from the formula Ag_3AsO_4 calculate the value of the solution in terms of arsenic.

Assume, for example, that 1 c.c. $\frac{N.}{10}$ $NH_4CNS = x$ gms. Ag, then

1 c.c. $\frac{N.}{10}$ $NH_4CNS = x \times \frac{324}{75}$ gm. As.

The Analysis.—Weigh out ·2 gm. (or suitable quantity) of the sampled and very finely powdered ore. Transfer to a square of glazed paper, and carefully mix with about 3 gms. of a mixture of finely powdered Na_2CO_3 and KNO_3. Transfer to a small porcelain crucible. Gradually heat to fusion and fuse for 4 or 5 minutes. Allow to cool. Add a little warm water; set in a 10 cm. porcelain basin containing a little water. Gently warm till the mass is dissolved. Remove from the heat. Wash the upper portion of the crucible (which may have fallen over on its side) with the wash jet. Remove the crucible on a glass rod, washing it down with the jet. The crucible may now be taken in the fingers and its interior examined, and any traces of the fusion removed by further treatment with water.

Acidify the filtrate with nitric acid and boil to expel any nitrous fumes and carbonic acid.

Cool and neutralise as follows:—Float a small piece of litmus paper in the liquid, and then add drop by drop 5E. NH_4HO until the litmus paper turns blue. Make slightly acid with one or two drops of 16E. HNO_3. Drop in a fresh piece of litmus paper and gradually add E. NH_4HO, so that on standing for half a minute the paper just turns blue.

If a considerable precipitate is thus formed, filter and wash well.

Now add a neutral solution of $AgNO_3$ in slight excess. Stir, and note the colour of the litmus paper. If red, again neutralise.

Filter off the red precipitate of arseniate of silver and wash well with cold water. Place under the funnel a 300 c.c. flask, and dissolve the precipitate with pure 5E. HNO_3. Wash the paper with distilled water acidified with HNO_3, bringing the total volume of the washings up to about 200 c.cs. Add 5 c.cs. of the iron-alum solution.

Titrate as before with $\frac{N.}{10}$ NH_4CNS. Repeat the estimation on a fresh portion of the ore. From the value of 1 c.c. calculate the percentage of arsenic present. With some practice this method will be found both accurate and rapid, therefore well suited for the work of the metallurgical chemist.

(*g*) THE VOLUMETRIC ESTIMATION OF MANGANESE BY POTASSIUM PERMANGANATE. (Volhard's Method).

Aparatus, Reagents.—The usual apparatus. For the standard solution $K_2Mn_2O_8$ is required. Zinc oxide free from Mn is used for neutralisation. For analysis the student may take a ferro-manganese ore (containing Fe and Mn).

Method, Reactions.—If a dilute, neutral or faintly acid solution of a manganese salt be heated to boiling, and a solution of $K_2Mn_2O_8$ added, a brownish red precipitate of hydrated MnO_2 is formed—

$$K_2Mn_2O_8 + 3MnSO_4 + 2H_2O = K_2SO_4 + 5MnO_2 + 2H_2SO_4$$

and as soon as the permanganate is in excess the characteristic rose colour appears. The reaction is exact in a neutral solution containing no iron or chromium, therefore excess of acid is to be avoided, and any iron and chromium present must be removed before titration. This condition is obtained by adding an emulsion of zinc oxide (pure) in slight excess, the acid being neutralised and ferric hydroxide precipitated.

Preparation of Standard Solution.—The $\frac{N.}{10}$ $K_2Mn_2O_8$ previously used for iron will serve again if any remain. If not prepare a $\frac{N.}{10}$ permanganate solution as before.

Checking the Standard.—If the solution previously used is available it should again be checked by titration against metallic iron (wire). If the solution be freshly prepared it will also be checked in this way—

1 c.c. $\frac{N.}{10}$ $K_2Mn_2O_8$ should equal ·00165 gm. Mn. The value in terms of Mn may be obtained by multiplying the value in terms of Fe by ·2946.

The Analysis.—Weigh out ·5 gm. of the sampled and finely powdered ore. Transfer to a casserole or porcelain dish. Add 2 c.cs. 10E. HCl, 4 c.cs. 16E. HNO_3, and 6 c.cs. 10E. H_2SO_4. Heat on the iron plate till dense white fumes are evolved, and continue at this heat about three minutes. Transfer the contents of the porcelain to a 500 c.c. flask. If any particles of the ore appear undissolved (of the original colour) repeat the acid treatment and combine the solutions. Wash out the casserole or dish with hot water, and to the contents of the flask add an emulsion of zinc oxide till the acid is neutralised and the iron is precipitated as $Fe_2(HO)_6$. Violent

agitation hastens the precipitation of the iron. Test the progress of the precipitation by removing a drop of the solution and adding to it in a small test tube a little of the zinc oxide emulsion. Shake, and notice if a precipitate forms. Pour back the test into the main solution.

When the precipitation is complete any appreciable excess of zinc oxide must be avoided.

Dilute with distilled water to the mark. Shake and let settle. When settled remove with a pipette 100 c.cs. of the clear liquid to a 300 c.c. flask. Heat to boiling over a flame, and titrate with $\frac{N.}{10}$ $K_2Mn_2O_8$, shaking after each addition until a permanent pink is obtained, visible at the edges of the clear liquid by holding a sheet of white paper behind the beaker. If this titration has taken some time the solutions should again be heated to boiling. If the pink tint disappears a little more $K_2Mn_2O_8$ is required.

If the percentage of manganese is low it will be advisable to take 200 c.cs. or more for titration. When titrating hot liquids the student must be careful that the steam does not appreciably heat the burette. As a rule, if the titration be performed quickly there is little danger of thus introducing error, but if prolonged the student had better make a connection leading sideways from the burette jet, so that the burette is not vertically above the rising steam.

The results of this analysis are calculated in percentages as usual, and should agree to ·1%.

Conclusion to Chapter VII.

Of the examples given of precipitation-volumetric methods the majority are in daily use by metallurgical chemists, and many of these methods, when employed intelligently, conform closely to the ideal typical method of technical analysis, the two leading demands of which are accuracy and speed. The student who has carefully and intelligently followed out the descriptions given should now be able to avail himself of the full store of information in the works mentioned throughout the text, and on studying these works he will obtain a fuller idea of the practical importance of this branch of volumetric analysis.

CHAPTER IX.

IV. COLORIMETRIC ANALYSIS.

This method of analysis is generally applied to the determination of small percentages of an element or compound, and in this chapter the following will be considered :—

(*a*) **The Colorimetric Estimation of Copper.**
(*b*) **The Colorimetric Estimation of Carbon in Steel.**

And though not coming under this head,

(*c*) **The Volumetric Estimation of Copper by Potassium Cyanide.**

This last method is of considerable importance to the metallurgical chemist, and, strictly speaking, cannot be introduced under any of the five heads laid down ; therefore, for convenience, it is introduced here.

(*a*) THE COLORIMETRIC ESTIMATION OF COPPER.

Apparatus, Reagents.—The usual apparatus, including two burettes or Nessler tubes. For preparing the comparison standard pure electrolytic copper is required. For analysis the student may obtain a sample of copper slag.

Method, Reactions.—A certain amount of pure copper is dissolved in a definite quantity of HNO_3, and a known amount of NH_4HO added. After dilution to a given volume, the solution is transferred to a burette. The slag is so treated that the copper is separated out, preferably in the metallic form, and this separated copper is treated exactly the same as the pure copper, and is transferred to another burette or tube without dilution. Distilled water is added to the assay solution till the colours in the two tubes are exactly the same. Note the volume of the assay solution ; and as the value of 1 c.c. of the comparison standard is known, the value of the assay solution is easily calculated.

This method was originated by Heine. For other colorimetric methods for copper consult the works of Beringer, Furman, and Sutton.

The Comparison Standard.—In a flask with a small funnel in its neck dissolve 1 gm. of pure electrolytic copper in the smallest possible quantity of nitric acid. When dissolved, dilute and transfer to the 1000 c.c. flask, and make up to the mark at 16° C.

Ten c.cs. of this solution contain ·01 gm. copper. To 10 c.cs. of this solution add 1 c.c. 16E. HNO_3 and 4 c.cs. 20E. NH_4HO. Transfer this solution to the Nessler tube, rinsing the beaker out with distilled water.

If a burette is used, the student must ascertain the volume of the burette from the 50 c.c. mark to the upper edge of the glass stopper. This may be

done by filling another burette with water to the 50 c.c. mark. Fill also the burette to be used to the same mark. See that the jet below the tap is empty. Now run the water from this burette into the other burette, emptying the last drops by blowing through. Read the increase in volume, which is equivalent to the capacity of the burette tested from the 50 c.c. mark to the stopper. The second burette may also be checked in this way. The object of this is to enable the student to read the volume of liquid in the burette from the bottom upwards, and not from the 50 c.c. mark.

The Analysis.—Assuming that the slag contains about ·2% of copper, 1 gram of the slag will contain ·002 gm. copper. Weigh out about 5 gms. of the slag, and treat as instructed in the Chapter on Slags (Estimation of Copper in Slags, Part III.). The copper is thus separated as Cu_2S. Wash thoroughly. Pierce the apex of the paper with a glass rod, and wash the precipitate through into a beaker. To the contents of the beaker add 5 c.cs. 16E. HNO_3. Heat till the Cu_2S is all dissolved. Then evaporate nearly to dryness to drive off excess of HNO_3. Now add 1 c.c. 16E. HNO_3 and 4 c.cs. 20E. NH_4HO.

Transfer this solution to the Nessler tube or burette, rinsing out the beaker with a little distilled water. Now compare the tint of the solution in this tube with that of the solution previously prepared from 10 c.cs. of the standard. Dilute the assay solution with water, a little at a time, shaking with the thumb on the end of the tube after each addition. Continue the dilution till the tint of the solution appears the same in the two tubes. Read the volume of the solution in each tube. (If a burette is used, suppose it reads 40 c.c., then the contents of the burette = $(50 - 40) + x = 10 + x$, where x = the contents of the burette between the 50 mark and the stopper.)

Calculation of the Results.—Assume that the 'standard' tube contains 22 c.cs. of standard solution, and that the 'assay' tube contains 25·5 c.cs. of solution when the tint is the same in each.

Now the 22 c.cs. of standard solution contain ·01 gm. copper, or 1 c.c. = $\frac{·01}{22}$ gm. copper.

Then each c.c. of the assay solution will have the same value. Therefore the assay solution contains $\frac{·01}{22} \times 25·5 = ·0116$ gm. copper, or $\frac{·0116}{5} \times 100 =$ ·232% copper.

(*b*) THE COLORIMETRIC ESTIMATION OF CARBON IN STEEL.

Note.—If the student cannot obtain a sample of standard steel (that is, of known carbon contents) of exactly the same manufacture and in the same physical condition as the sample to be analysed, this estimation may be omitted until the student comes to the section dealing with Technical Analysis (Part III.).

Apparatus, Reagents.—For comparing the tint of the assay and standard solutions two 'carbon tubes' are required. These are plain tubes closed at one end, and graduated from the closed end upwards in c.cs., generally from 0 c.cs. to 30 c.cs. For solution of the steel, two test tubes 150 mm. × 16 mm. are required, and for a water bath a beaker covered with a tin lid, through which two round holes 17 mm. diameter are made, may be prepared. Pure nitric acid free from Cl or HCl is used for dissolving the steel. The most suitable acid is one of S.G. 1·2.

Method.—The following method was first introduced by Eggertz in 1862 :—

When steel is dissolved in nitric acid, the carbon which sometimes at first separates out is at length dissolved and colours the solution brown, and by comparing the depth of colour with that obtained from a standard steel the carbon contents may be ascertained.

To secure accuracy, it is essential that the standard steel should be of the same kind and in the same physical condition as the sample to be examined. For instance, if examining a Bessemer steel, the standard steel should be Bessemer; and if the example examined has been hammered, tempered, or otherwise treated, the standard should have been subjected to the same treatment.

This method, then, is of much service when a large number of steels of one kind have to be tested. For the standard a sample of the kind under examination is taken, and the percentage of combined carbon is determined by the combustion method (see Technical Analysis, Part III.). Once the combined carbon has been accurately estimated in this way in a particular steel, hundreds of analyses of similar steels may be quickly performed without the tedious combustion, using the standard for comparison.

The student must remember, however, that a fresh standard must be used when dealing with a fresh kind of steel. It would lead to inaccurate results if, for instance, a standard Bessemer steel were used when examining an open-hearth steel. For further information the student is referred to *The Chemical Analysis of Iron*, by Blair.

The Standard Steel.—As before mentioned, unless the student can obtain a sample of the same kind of steel as that which he is going to examine and knows the carbon contents of the standard, this estimation should be postponed until he is able to make the necessary combustion analysis. Then he will be able to ascertain the combined carbon contents of a steel; and taking this as a standard, he can proceed to examine other steels of the same kind by the colorimetric process.

The Analysis.—Weigh out carefully ·2 gm. of the standard steel (drillings) and ·2 gms. of the sample to be analysed. Transfer each sample to a test tube. Fill the beaker nearly half full of cold water. Cover with the tin lid, and insert the two test tubes through the holes. The steel is now to be dissolved in pure nitric acid of S.G. 1·2. If the steel is supposed to contain less than ·3% carbon, use 3 c.cs. HNO_3; between ·3% and ·5%, 4 c.cs.; between ·5% and ·8%, 5 c.cs.; between ·8% and 1·0%, 6 c.cs.; over 1%, 7 c.cs., and over 1·75%, 8 c.cs.

The right amount of HNO_3 is now dropped slowly into each test tube, and then in the top of the tube is placed a small glass funnel. Place the beaker and tubes on an iron plate and heat to boiling. Boil till all the carbonaceous matter is dissolved. The time of boiling varies according to the carbon contents of the steels, and runs from twenty minutes with ·2% to forty-five minutes with over 1% carbon. The absence of small bubbles and the disappearance of any flocculent matter indicate complete solution. The tubes during the solution should be shaken now and then, to prevent the formation of a film of iron salts or oxide on the tube. Also the student must see that the solutions are not exposed to direct sunlight, which weakens the colour.

Now pour the standard solution into one of the carbon tubes, washing out the test tube with a little cold distilled water. Dilute to 10 c.cs. Pour the assay solution into the other carbon tube, wash out the test tube with a little cold distilled water. Compare the colours, holding the two tubes together in front of a sheet of white paper held against the light. Dilute the

assay solution, shaking after each dilution, till the tint exactly matches that of the standard solution. Read the volume of the assay solution.

Calculation of Results.—Assume that the standard steel contains ·32% combined carbon, and that the solution of the ·2 gm. sample of the standard steel was made up to 10 c.cs., and that when the tints of the solutions exactly matched the volume of the assay solution was 16·6 c.cs., then the percentage of combined carbon in the steel is $\frac{·32 \times 16·6}{10} = ·5312\%$.

The student should continue his practice on the same sample of steel till the results do not differ by more than ·02%.

(*c*) THE VOLUMETRIC ESTIMATION OF COPPER BY A STANDARD SOLUTION OF POTASSIUM CYANIDE.

Apparatus, Reagents.—The usual apparatus. For the preparation of the standard solution pure KCN (gold cyanide, 98%) is best, and for checking the standard, pure electrolytic copper foil is used. For precipitating the copper in the assay solution the sheet aluminium used in the iodide assay will again answer the purpose. For analysis the student may take the same sample as used previously for the iodide method.

Method, Reactions.—When ammonia is added to a solution of cupric nitrate a deep blue solution is formed, probably containing the compound $Cu(NO_3)_2,4NH_3$. On adding to this solution a solution of KCN the dark blue colour disappears. The exact nature of this reaction seems to be a matter of some doubt; probably a double cyanide of ammonia and copper or potassium and copper is formed together with certain organic compounds formed by the complex reactions of the ammonia and cyanogen liberated (Liebig). Whatever the chemical reaction may be, their result is clearly evident; and by measuring the volume of KCN required, the percentage of copper present can, if the value of the KCN solution is known, be easily calculated.

Regarding the details of the analysis, the student will find on consulting Beringer and Sutton that some care is necessary when dealing with ores. The method here given is a modification due to A. H. Low (of Denver, Colorado), and as in it the copper is separated practically free from the ordinary impurities of copper ores, the effect of these impurities need not be considered; but to ensure success the following points should be noted:—

1. For the same amount of copper, a concentrated solution requires more KCN for decoloration than a dilute one; therefore always work with approximately the same volume of solution.
2. A hot solution requires for the same amount of copper less KCN than a cold one, therefore always titrate at about the same temperature, say 16° C. to 20° C.
3. For the same amount of copper the volume of KCN will vary according to the time taken for the titration; therefore cultivate a uniform rate of titration for all cases.
4. As far as possible, weigh out such quantities of ore that approximately the same quantity of copper is always present in the assay solution. Also see that the final volume after titration is approximately the same in all cases.
5. See that the same quantities of acid and ammonia are present in the assay solution as were used in the solution of metallic copper for standardising the KCN solution. In general, see that all the conditions of standardisation are the same as those in the actual analysis.

The Standard Solution.—In practice the solution generally employed is of such a strength that 1 c.c. = ·005 gm. copper. To prepare this solution weigh out 25 gms. 'gold cyanide.' Dissolve in distilled water and make up to one litre.

Checking the Standard.—Weigh out, in duplicate, about ·2 gm. pure, clean, copper foil. Transfer each to a 300 c.c. flask. Add 5 c.cs. pure 16E. HNO_3. When the copper is all dissolved add 80 c.cs. distilled water and then 10 c.cs. 20E. NH_4HO. Cool under the tap and then titrate with the KCN solution. The student should roughly calculate how many c.cs. he will require. There is less danger then of overstepping the mark. At first run in 1 c.c. at a time and shake, and when about three-quarters the approximate quantity has thus been run in reduce the volume of each addition till finally, as the colour fades to a pale lavender, the solution is being added drop by drop; add water to bring the volume to 150 c.cs.; continue till the lavender colour is no longer seen on holding the flask against a sheet of white paper. The student should note the exact tint to which he is working, as he must titrate the assay solution to exactly the same degree.

Calculate the value of 1 c.c. of the KCN solution. The duplicates should agree within ·00005 gm. copper.

The Analysis.—Weigh out such a quantity of the sampled and finely ground ore as will contain about ·2 gm. copper. Pure copper pyrites contains about 30% copper, therefore ·6 gm. will contain ·2 gm. copper. With other ores the student must depend on his mineralogical knowledge, and until he gains experience he must frequently adjust the weight of ore largely on guesswork. The results of one analysis will, however, guide him when running the duplicate. Treat the ore exactly as was done in preparing the solution for the iodide assay, proceeding with the treatment until the copper is obtained precipitated in the metallic form by aluminium. After washing as before, dissolve in 5 c.cs. 16E. HNO_3, add 80 c.cs. distilled water and 20 c.cs. 20E. NH_4HO. Cool and titrate as before, making the bulk up to 150 c.cs. when the colour becomes faint.

Note the number of c.cs. used and repeat the estimation. Calculate the percentage of copper as usual. The results should agree within 0·1%.

Note.—The aluminium precipitation is in the older methods omitted, consequently on adding NH_4HO when iron is present a heavy precipitate of $Fe_2(HO)_6$ is formed. If this be filtered off it is impossible to wash it free from copper, hence it is advisable to titrate with it present, but only on the condition that the cyanide solution has been standardised with a similar amount of iron present. For details consult Sutton. Used with this precaution, this modification gives with some practice results accurate within ·2%, but where a higher degree of accuracy is required, the method just laid down (Low's) should be followed. The results so obtained are sufficiently accurate for ordinary work, but where absolute accuracy is required the Iodide or Electrolytic methods are preferred.

CHAPTER X.

GASOMETRIC ANALYSIS.

Of this type of analysis only one example will for the present be given, as the subject will again be considered in Part III.—"The Analysis of Furnace Gases."

Apparatus, Reagents.—The special piece of apparatus termed the nitrometer is shown in fig. 69, and consists of two vertical glass tubes *a* and *b*, connected at the foot by a length of stout-walled rubber tubing *c*, and attached by clamps to a suitable stand. The tube *b* is plain, but the tube *a* is graduated from the top downwards, usually in 50 c.cs. divided in tenths. The top of this tube is contracted and terminated in a tap (Greiner and Friedrich's patent), surmounted by a funnel *d* and a capillary tube *e*. By this tap the tube may be connected to either the funnel or capillary, or may be disconnected from both.

Various forms of nitrometer are in use (see Sutton), but for the present the student may employ the form just described.

For analysis the student may take a sample of potassium nitrate and estimate the percentage of NO_3 present. For this purpose quicksilver will be necessary for the measuring liquid, and in reading its volume the student may read the top of the meniscus.

Method, Reactions.—When strong H_2SO_4 is added to a solution of KNO_3 the following reaction occurs,

$$KNO_3 + H_2SO_4 = HNO_3 + KHSO_4$$

the acid sulphate being formed, and in the presence of mercury the nitrogen is liberated as nitric oxide, NO.

$$2KNO_3 + 3Hg_2SO_4 + 4H_2SO_4 = K_2SO_4 + 6HgSO_4 + 2NO + 4H_2O.$$

From the measured volume of NO the percentage of NO_3 present may be calculated.

101 gms. KNO_3 contain 30 gms. NO, or 1 gm. KNO_3 contains $\frac{30}{101} = \cdot 297$ gm. NO.

But 1 litre NO at normal pressure and temperature weighs $\cdot 0896 \times \frac{16+14}{2} = 1 \cdot 344$ gms., therefore the volume of $\cdot 297$ gm. NO at normal temperature and pressure will be $\frac{1000 \times \cdot 297}{1 \cdot 344} = 221$ c.cs. That is, 1 gram of pure KNO_3 will produce 221 c.cs. of NO at normal temperature and pressure. Then 1 c.c. of NO under these conditions will correspond to $\frac{1}{221} = \cdot 00452$ gm. KNO_3, or $\cdot 00452 \times \frac{62}{101} = \cdot 00277$ gm. NO_3.

Measurement of Gases.—To obtain a correct reading of the volume of a gas, the following factors have to be taken into account:—

1. *The Temperature of the Gas.*
2. *The Pressure of the Gas.*
3. *The Aqueous Vapour present.*

1. **The Temperature of the Gas.**—As the volume of a gas varies directly as the absolute temperature T (= centigrade temperature + 273) when the pressure is constant, then, if the temperature at which the volume of the gas is read is $t°$ C., and V = the volume at $t°$ C., then the volume V_0 at 0° C. is obtained thus,—

$$V_0 = V \cdot \frac{273}{273+t}, \text{ or } V_0 = V \cdot \frac{T}{T_1}, \text{ where T and } T_1$$

are the absolute temperatures at the centigrade temperatures 0° and $t°$ respectively.

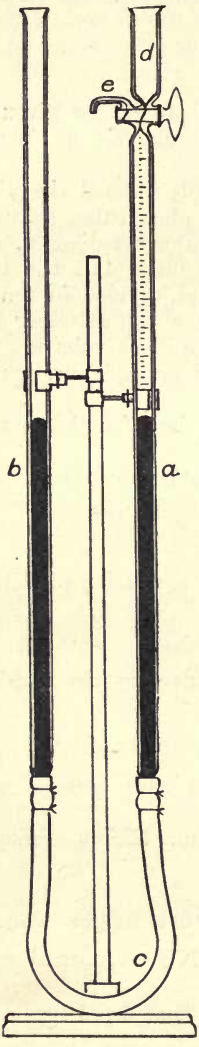


FIG. 69.

2. **The Pressure of the Gas.**—When the temperature of a gas is constant the volume varies inversely as the pressure. This pressure, being in the analysis considered as that due to the atmosphere, is taken as the height of the barometer in millimetres, the standard pressure being taken at 760 mm. Then if V_0 be the volume at 760 mm. and V be the volume read in the analysis at a barometric pressure P_1,

$$V_0 = V \times \frac{P_1}{760} \quad or \quad V_0 = V \times \frac{P_1}{P}$$

where P_1 = pressure in analysis and P = standard pressure.

Combining 1. and 2. we get

$$V_0 = V \times \frac{P_1 T}{P T_1}$$

For example, find the volume at standard temperature and pressure of 20 c.cs. at 17° C. and 770 mm. barometric pressure.

$$V_0 = 20 \times \frac{770 \times 273}{760 \times 290} = 19{\cdot}07 \text{ c.cs.}$$

3. **The Aqueous Vapour present.**—If any aqueous vapour (moisture or humidity) be present in the gas measured it exerts a pressure against the pressure of the atmosphere (barometric pressure), therefore the volume of a gas is increased if aqueous vapour be present. For the student's purpose he may take the pressure or tension of aqueous vapour from the following table; for very accurate work, however, he should refer to the tables given in physical text-books.

°C.	mm.	°C.	mm.	°C.	mm.
15	12·7	18	15·4	21	18·5
15·5	13·1	18·5	15·8	21·5	19·1
16	13·5	19	16·3	22	19·7
16·5	14·0	19·5	16·9	22·5	20·2
17	14·4	20	17·4	23	20·9
17·5	14·9	20·5	17·9	23·5	21·5
				24	22·2

Thus, for example, if a gas contain aqueous vapour and be at a temperature of 18° C., this aqueous vapour will exert a pressure of 15·4 mm. against the barometric pressure; therefore, in making the necessary calculation, this quantity must be subtracted from the barometric reading, and the correction formula now becomes—

$$V_0 = V\frac{(P_1 - P_2)T}{PT_1}$$

where P_2 = the pressure or tension of the aqueous vapour. Thus, in the example just given,

$$V_0 = 20\frac{(770 - 14{\cdot}4)273}{760 \times 290} = 20\frac{755{\cdot}6 \times 273}{760 \times 290} = 18{\cdot}72 \text{ c.cs.}$$

The Analysis.—Raise the tube *b* and into it pour quicksilver until it just reaches the glass tap in *a* and fills the bottom two inches of *b*. This condition is obtained by raising or lowering the tube *b* as may be required. Close the tap and clamp *b*. Weigh out ·1 gm. KNO_3. Transfer to the funnel. Add 2 to 4 c.cs. of water, and when dissolved open the tap, connecting the funnel to *a*, and gently unclamp and lower *b* till the liquid has passed into *a*. Rinse the funnel with about 1 c.c. of distilled water from a wash bottle with a fine jet. Again lower *b* till the wash passes into *a*. Then rinse the funnel with 3 c.cs. 36E. H_2SO_4, running it down a glass rod against the sides of the funnel. Again lower *b* till the acid passes into *a*. Quickly add another wash of 3 c.cs. 36E. H_2SO_4. Close the tap when the wash is transferred to *a*. If any air has been enclosed during these operations it should be removed by raising the tube *b* slightly and gently opening the tap, and when the air has escaped the tap is closed.

Unclamp *a*; incline it in both hands almost horizontally, and with a quick motion bring it back to the vertical. Repeat this process for two or three minutes, so that the mercury and the acid are well mixed. Now adjust the tubes in the clamps so that the mercury in *a* is approximately at the same level as that in *b*. Allow to stand till the temperature coincides with that of the room. Now carefully adjust the tube *b* so that the mercury in it is higher than that in *a* by 1 mm. for every 6·5 mm. of solution in *a*. This makes the necessary allowance for the short column of liquid in *a*. Read the volume of gas in *a* (call this V).

Open the tap. The level of the mercury should not alter. Raise *b* so that the liquid passes into the funnel. Take the temperature of the liquid (call this *t*° C.) and read the height of the barometer (call this P_1).

From the table obtain (by interpolation if necessary) the vapour pressure corresponding to the temperature *t*° C. Then by the formula—

$$V_0 = V \times \frac{(P_1 - P_2)T}{PT_1}$$

calculate the volume of the gas at normal temperature and pressure.

Multiply this volume by the value of 1 c.c. of NO in terms of NO_3 (1 c.c. = ·00277 gm. NO_3) and the quantity of NO_3 present is obtained. The percentage is calculated as usual.

Note.—When estimating the NO_3 in KNO_3 or $NaNO_3$ it is more convenient to use the modified (Lunge's) form of nitrometer of large capacity. Larger quantities of nitrate may then be taken for analysis.

Further information regarding the use of the capillary tube will be found in Sutton's *Volumetric Analysis.*

In Part III. the Hempel burette will be described, and the student should note that with it, as the volumes read are relative and the conditions nearly uniform, it is not necessary for general work to make the temperature and other corrections just described. In the time taken for the analysis the fluctuations in these are, with care, but slight.

CHAPTER XI.

ELECTROLYTIC ANALYSIS.

THE theory of electrolysis cannot be taken up at any length here, and the student desiring fuller information on this subject is referred to the works of Ostwald, Nernst, James Walker, and others. Briefly, it may be stated that on passing a current of electricity through a solution of a salt in water the salt is broken up. This process is termed **electrolysis.** The conductors connected to the two battery terminals are called **electrodes**; that connected to the zinc of an ordinary cell being termed the **negative electrode** or **kathode,** and that with the other terminal the **positive electrode** or **anode.**

The free positive and negative radicals produced by the action of water on salts are termed **ions** (things that go); *e.g.* on dissolving **NaCl** in water the sodium chloride is split up, if the solution be very dilute, into the ions **Na** and **Cl**, the **Na** carrying a charge of positive, and the **Cl** a charge of negative electricity; and the amount of electricity carried by the **Na** ion is equal to that carried by the **Cl** ion, but opposite in sign, hence the solution as a whole is electrically neutral.

But on introducing the electrodes and passing a current, one electrode is charged with positive electricity and the other with negative. The positive ion travels to the negative electrode and the negative ion to the positive electrode. The **Cl** ion, for instance, travels to the positive electrode or anode; there it gives up its negative charge, and two of the uncharged **Cl** ions unite to form the molecule Cl_2, a gas. The **Na** ions with their positive charges travel to the kathode and are there relieved of their electrical charges. The metallic sodium thus formed at once reacts with the water present, forming **NaHO.** That is, the products of the electrolysis of a solution of **NaCl** are chlorine gas and caustic soda.

The ions charged with positive electricity are attracted by the negative electrode or kathode and are termed **Kathions** (Cathions). Hydrogen and the metals come under this head.

Those charged with negative electricity wander to the positive electrode or anode and are termed **Anions.** The acid radicals belong to this class.

It must be remembered that these ions existed in the solution before the current was passed; the current merely collects them at the electrodes according to their respective charges of electricity—whether positive or negative.

In conducting analysis by electrolysis the following points must be considered:—

1. *Production of the Current.*
2. *Measurement of the Current Strength.*
3. *Measurement of the Tension.*
4. *The Electrodes and Electrolytic Cell.*

1. **Production of the Current.**—Various forms of cells, primary and secondary, and dynamos, may be used for the production of the current. For the student's purpose, however, two quart Daniell cells will suffice. Each of these consists of a large glass jar containing a copper cylinder (or simply an outer copper cylinder) and filled with a saturated solution of sulphate of copper, the crystals being present in considerable excess. Inside the copper cylinder is placed a porous earthenware pot, containing dilute sulphuric acid, and a zinc rod, amalgamated liberally by rubbing under dilute acid with mercury. On immersing the zinc rod in the sulphuric acid (1 of 36E. H_2SO_4 to 12 parts water) it should not produce a brisk effervescence.

The two cells are connected up thus: the wire from the zinc of one cell is connected to the copper of the next. The two free terminals—a copper and a zinc—are connected by wires direct to the electrodes, the wire from the zinc being connected to the kathode and the wire from the copper to the anode.

For other methods of generating the current and other details concerning electrolytic analysis the student is referred to the excellent treatise of Drs Classen and Löb (translated by Herrick and Boltwood) on *Quantitative Chemical Analysis by Electrolysis.*

2. **Measurement of the Current Strength.**—Just as in estimating the work done by water we consider the quantity of water and the head or pressure, so here we consider quantity and tension or pressure, the quantity of the current being measured in *amperes* and the tension (or pressure) in *volts.* The exact value of these units is given in any elementary text-book on electricity. Under this head the measurement of the current (or quantity of electricity) is considered.

In order that the student may know exactly the conditions under which he is working, the current should be measured by an ampere-meter (ammeter) with a range of 0 to 6 amperes. To check the current strength this instrument is introduced into the circuit and the quantity of electricity in amperes is read direct from the dial of the ammeter.

To reduce the current a resistance box may be introduced into the circuit, and to increase the current, if cells are used, a number may be connected in parallel, that is, all the zincs are connected together and all the coppers, and a leading wire is taken from each group to the electrodes.

The student is advised not to attempt to procure the current from electric mains, either power or lighting, unless acquainted with the properties of electricity, and the necessary adjustments required to regulate these strong currents to his requirements. (He may investigate the suitability or otherwise of alternating currents for electrolytic analysis.)

3. **Measurement of the Tension.**—That this may be accurately ascertained, it is advisable that the student procure or obtain the use of a voltmeter such as Weston's, which gives values accurate to $\frac{1}{10}$th volt, the voltage being read direct from the dial.

To increase the tension with cells, connect up a number of them in series, that is, zinc to copper, zinc to copper, and so on. If at the same time it is desirable to increase the current strength or amperage, connection by series parallel may be resorted to. For example, 16 cells may be connected thus: Connect 4 cells in parallel, then other 4, and so on till 4 sets of 4 cells each in parallel are obtained. Then consider each set as a single cell, and connect the zinc of one set to the copper of the next and so on.

A convenient method of lowering the tension is by the introduction of a shunt circuit. If the two poles of a cell or other source of current be connected by a wire, and a loop of similar wire be connected to two points

in this wire some distance apart, then part of the current flows through the main wire and part through the loop, and the tension in the loop is to the tension between the two terminals as the distance apart of the loop connections is to the length of the main connecting wire, assuming the wire of equal cross section and uniform throughout.

4. **The Electrodes and the Electrolytic Cell.**—If special electrodes are not available the student may use a large platinum dish or crucible for the kathode, and for the anode a platinum wire, terminating somewhat as shown in fig. 70*b* (see next page). It is, however, recommended that the electrodes to be described be purchased or manufactured from thin sheet platinum and platinum wire.

The condition of the precipitate formed by electrolysis depends greatly on the strength of current flowing through the cell. A current of twice the strength will precipitate twice the quantity of metal in a given time. The strength of current therefore determines the rate of deposit on the electrode.

This being so, the size and shape of the electrodes become a matter of importance. If the area of an electrode is small and the current density high, the atoms of metal are deposited in such rapid succession, crowding together, that a coherent precipitate is not obtained; and as in electrolytic analysis the precipitate is generally to be weighed on the platinum electrode, a non-coherent precipitate cannot be expected to give good results. Again, with the opposite extreme—large electrode surface and low current strength —the coating will be patchy, and again unsatisfactory.

It is evident, then, that some mean between these extremes should give the best results. A convenient standard of measurement is that adopted by Dr Classen, the current density being always given with reference to 100 square centimetres of electrode surface. Thus, if a platinum cylinder 2·5 cm. × 7·5 cm. be used as the kathode, and dip 5 cm. in the solution to be electrolysed, then the surface available is $2{\cdot}5 \times \frac{22}{7} \times 5 \times 2 = 78{\cdot}6$ sq. cm. Suppose the ammeter shows that 1·2 amperes flow through the cell, then every 100 sq. cms. receive a current of $1{\cdot}2 \times \frac{100}{78{\cdot}6} = 1{\cdot}52$ amperes. Classen adopts the symbol ND_{100} to represent the current density per 100 sq. cms. electrode surface. In the example, then, $ND_{100} = 1{\cdot}52$ amperes.

When determining metals it is sufficient to know the current density at the kathode alone, but when determining the halogens and other elements or compounds deposited on the anode, it is important that the current density at the anode be known. As a rule, a current density of ND_{100} = ·5 to 1·5 amperes is most suitable, though exceptions on both extremes are met with. The tension, as a rule, runs from 1 to 4 volts.

The most convenient form of kathode is a plain platinum cylinder, as shown in fig. 70*a*.

Length, 7·5 cm.; diameter, 2·5 cm.; length of connecting platinum wire, 12 cm. This wire is riveted to the cylinder, which is more convenient if cut down the side opposite to the wire. This allows of the easy removal of the kathode without previous removal of the anode. The weight of the kathode is about 15 to 18 gms.

The anode is made of platinum wire about 1 to 1·5 mm. in diameter. Length of straight stem (see fig. 70*b*) is about 20 cm. At the base, as shown in the figure, this wire terminates in a coil about 3 cm. in diameter, the folds of the coil being spaced about 3 mm. apart. This form of anode

ensures a uniform evolution of gas, and an even deposit on the kathode both inside and outside.

It is essential to success that the student exercise great care in keeping the surfaces of the electrodes *clean*, otherwise an even metallic coating cannot be obtained. The kathode surface must be perfectly free from any greasy matter. It is also essential that all metallic connections in the circuit be kept bright and clean, or the current may be weakened or broken.

For the support of the electrodes the two stands shown in the figure may be used, the anode being attached as shown to the one and the kathode to the other, the stands and electrodes being adjusted in the position shown. A single stand with suitable connection may be substituted, or one of the racks (for a number of assays) described in the works of Beringer or Peters (Copper Smelting). The wires from the battery are attached as shown in fig. 71.

For the electrolytic bath a narrow deep glass beaker of 200 c.cs. to 250 c.cs.

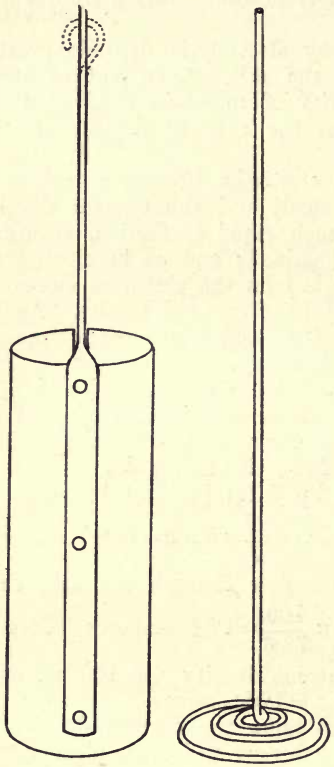


FIG. 70*a*.

FIG. 70*b*.

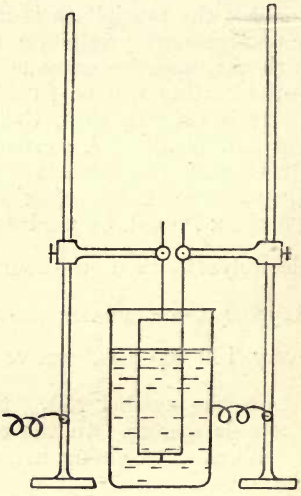


FIG. 71.

capacity is most suitable. With this form of beaker, if not filled more than two-thirds full, there is little danger of small particles of the solution being thrown over the edge by a rather brisk ebullition of gas.

Before proceeding to an analysis, the apparatus must be thoroughly cleaned, the necessary source of current prepared, and the apparatus connected up as follows:—Having charged two or three quart Daniell cells, connect them in series. If an ammeter and a voltmeter are available, the former may be connected to the free zinc terminal and the latter to the free copper terminal, and from each of instruments a wire is connected to the two standards shown in the last figure. The electrodes are then connected—the kathode to the zinc end of the battery—and the apparatus is ready for the electrolysis of the solution, which is placed in the bath described.

If the measuring instruments are not available, the free copper and zinc terminals are connected direct to the electrodes. Regarding the ammeter and voltmeter, it is advisable that they be removed, except when it is desired to measure the current. On removing the ammeter, its place in the circuit should be filled with a wire (or resistance roll) of the same resistance as the ammeter, otherwise the conditions of the analysis would be slightly different when the instrument was removed.

The voltmeter is best introduced into the circuit by joining a wire to the wire connected to the kathode and then to the voltmeter. The other binding screw of the voltmeter is then connected by a wire to the copper terminal of the battery, there being therefore two wires coming from the copper terminal and one from the zinc. All these connections should be made with wire at least 1·5 mm. in diameter.

THE ELECTROLYTIC ESTIMATION OF COPPER.

(*a*) **In pure copper sulphate.**

(*b*) **In a copper ore.**

(*a*) IN PURE COPPER SULPHATE.

The apparatus described will suffice for this estimation. Good results may be obtained without the use of the ammeter, voltmeter, and resistance boxes, though it is advisable that the student should if possible ascertain definitely the conditions of the experiment.

For analysis, the student may take a sample of the pure sulphate $CuSO_4,5H_2O$ previously prepared.

Method of Analysis.—The copper sulphate is dissolved in distilled water, and nitric acid added in not greater quantity than 5% by volume. On diluting the solution sufficiently the copper sulphate is split up into the kathion **Cu** and the anion SO_4. The discharged **Cu** is deposited on the kathode, and the discharged sulphate radical attacks the water thus:—

$$2SO_4 + 2H_2O = 2H_2SO_4 + O_2$$

It must be remembered that on electrolysis HNO_3 splits up thus—

$$2HNO_3 = H_2 + NO_3$$

and this hydrogen acts as a reducer on the HNO_3 thus—

$$4H_2 + HNO_3 = NH_3 + 3H_2O$$

and in the presence of sulphuric acid or a sulphate the final product is ammonium sulphate.

On prolonged passage of the current, if iron or zinc be present, these salts would be broken up and their hydrated oxides deposited on the kathode.

The presence of chlorides must be avoided.

Best conditions of experiment—(Classen):—

Temperature, 20°–30° C.
Current density, $ND_{100} = 0{\cdot}5$ to 1 ampere.
Electrode tension, 2·2 to 2·5 volts.
Volume of solution, for 1 gm. sulphate about 120 c.cs.
Time, 4 to 5 hours.

The Analysis.—Weigh out 1 gm. of the sulphate which has been dried between sheets of filter paper. Transfer to a deep narrow 200 c.c. beaker. Add 100 c.cs. distilled water and 5 c.cs. 16E. HNO_3. Make up to 120 c.cs. with distilled water.

See that the electrodes are thoroughly clean. Remove the kathode. Rinse with 5E. HNO_3, then with distilled water, and finally with absolute alcohol. Gently ignite in a low bunsen flame till dry. Remove in the desiccator and weigh when cool. Replace the kathode. Bring up the beaker, raising it on a block till the electrodes dip about 6 to 7 cms. in the liquid. See that the anode does not touch the kathode, and is uniformly set with regard to it.

Allow the current to pass. A brisk stream of bubbles should rise from the coil and stem of the anode. If these do not appear or are very sluggish see that the battery cells are properly charged and that *all* connections are clean and properly made.

Continue passing the current for four or five hours, when the solution should be almost colourless. The end of the reaction is determined by removing about $\frac{1}{2}$ c.c. of the solution by a pipette and testing in a small test tube with NH_4HO or H_2S (the latter can only be used if no other reacting elements are present), or lower the electrodes and notice if a fresh deposit forms. Draw off the solution with a pipette and wash down the kathode at the same time with distilled water. Fill a deep narrow 250 c.c. beaker with distilled water. Unclamp the kathode and remove it quickly to the water in the beaker. Remove the kathode from this beaker into another containing pure alcohol. Remove from the alcohol and gently heat in a low bunsen flame till dry.

Remove in the desiccator; cool and weigh. The difference between this weight and that of the kathode gives the weight of copper deposited. Compare the results of duplicates with those previously obtained.

Note.—To prepare the kathode for the next estimation, place in it a 250 c.c. beaker and add about 160 c.cs. 5E. HNO_3 to remove the copper. Wash, dry, and weigh as before.

(*b*) THE ESTIMATION OF COPPER IN ITS ORES.

The necessary apparatus is the same as before. For analysis the student may take a sample of the ore previously used for the cyanide and iodide estimations of copper.

Method, Reactions.—After the preliminary treatment of the ore the copper is separated as before. If iron and zinc are present in the solution the current should not be passed longer than is necessary to effect the complete deposition of the copper, or the nitric acid present will be reduced and ammonia compounds formed, resulting in the deposition on the kathode of the hydrated oxides of iron and zinc. If the method to be described be closely followed the copper may be completely deposited from solutions containing iron, alumina, zinc, nickel, cobalt, chromium, manganese, cadmium, calcium, barium, strontium, and magnesium.

Mercury, silver and bismuth would, if present in the solution, be deposited along with the copper.

The Analysis.—Weigh out 1 gm. of the finely powdered and sampled ore. Transfer to a 250 c.c. beaker. Moisten with a little cold water. Add 25 c.cs. 16E. HNO_3 and 10 to 15 drops 36E. H_2SO_4. Cover with a clock glass and heat on the hot plate till all the ore is in solution and the nitrous fumes have disappeared. Wash the clock glass into the beaker and

evaporate the solution till dense white fumes of SO_3 freely come off. The copper now exists as sulphate. Set aside to cool for a few minutes, and when sufficiently cool add, cautiously, 10 c.cs. 5E. HNO_3, 4 drops 36E. H_2SO_4, and 40 c.cs. distilled water. Heat on the hot plate till the mass is in solution (neglect any insoluble matter). Filter off the insoluble matter through a small filter. Wash thoroughly, keeping the bulk of the washings and solution below 120 c.cs.

As a precaution it is advisable to quickly dry and incinerate the filter and contents and treat the ash with 2 c.cs. 16E. HNO_3. Evaporate in the porcelain crucible till nearly dry, and take up with 5 c.cs. water. Filter through a 5 cm. filter. Wash once or twice and add the solution to the main solution. Any copper contained in globules of sulphur or in the filter paper is thus collected.

The solution is now electrolysed as before and the copper present estimated. Repeat the estimation. Duplicates should agree within ·03% on ores running from 20% to 60% copper, and within ·02% for ores containing less than 20% copper.

THE ELECTROLYTIC ESTIMATION OF COPPER AND NICKEL IN A COPPER-NICKEL ALLOY.

The apparatus necessary is the same as before. For analysis the student may procure a nickel coin or other alloy of copper and nickel.

Method, Reactions.—The copper and nickel are obtained in solution as sulphates, and from the acid solution the copper is precipitated as before. After removal of the copper the solution is neutralized with ammonia, and excess of the same reagent is then added. The nickel is then precipitated on a clean kathode. Current density ND_{100} = 0·5 to 1·5 amperes (Classen) and electrode tension 2·8 to 3·3 volts.

This method may be used for copper ores containing nickel (see the article on the "Determination of Copper by Electrolysis," by Francis L. Sperry, in *Modern Copper Smelting* by E. D. Peters, Jnr.).

The Analysis.—Roll out the coin in a pair of rolls or hammer it thin on a clean anvil. Clip it into thin strips with a pair of strong scissors or shears. Weigh out about ·5 gm. of the clippings. Transfer them to a deep narrow 250 c.c. beaker. Add 20 c.cs. 5E. HNO_3 and warm till the coin is dissolved. Add 8 c.cs. 18E. H_2SO_4 and evaporate on the hot plate till all the nitric acid is removed.

Take up with 120 c.cs. distilled water and electrolyse as before, the most suitable conditions being as follows — Current density, ND_{100} = 1 ampere, and the electrode tension 2·75 to 3 volts.

When the copper is all deposited, remove, wash, dry and weigh the kathode. On removing the kathode it should be quickly washed into the beaker containing the solution, by means of a jet of water from the wash bottle. Note the weight of copper deposited.

Clean the kathode. Replace it. Neutralise the solution with ammonia and add an excess of 10 c.cs. 20E. NH_4HO.

Pass the current till the nickel is all deposited. The end of the reaction is ascertained by testing with ammonium sulphide or potassium sulphocarbonate. The coating on the kathode should be thick and bright.

Remove, wash, dry and weigh the kathode, and note the weight of the deposited nickel.

Concluding Note.—The examples given will be sufficient to give the student some practice in this branch of analysis. Further examples will be met with under "Mixed Analysis." (See "Smaltine for Nickel and Cobalt.").

CHAPTER XII.

"MIXED ANALYSIS."

The analyses dealt with in this chapter are all complex, involving the determination of at least two or three and very frequently more elements; and as these estimations may be carried out by pure gravimetric, electrolytic, volumetric, gasometric, or other methods, the term 'Mixed' has been applied to them.

One point must be rigidly insisted on, namely, that a careful qualitative analysis be performed before proceeding to the quantitative analysis. If this point be rigidly enforced it will lead in many cases to a considerable shortening of the quantitative work, and will much increase the probable accuracy of the results. Certain elements which may interfere with certain methods will be detected in time, and the scheme of operations modified accordingly. The student must remember that although some text-book lays down a 'scheme' for the analysis of some mineral, say a complex sulphide, this scheme must not be rigidly followed unless he has ascertained that the ore he is treating is similar in description to that to which the 'scheme' applies. He may find fewer or more elements present than those mentioned in the 'scheme,' and must therefore modify the scheme to suit each particular ore.

It is by no means intended that the student shall take liberties with the instructions given. He must cultivate self-reliance, and intelligently consider the methods applicable to any particular case; and the foundations necessary are a good knowledge of theoretical chemistry, qualitative analysis, and the methods of quantitative analysis.

It has been a matter of some difficulty to decide what estimations shall be included in this chapter; and though a somewhat limited number of analyses are given, those included have been selected as particularly suitable to the needs of the metallurgical student.

The estimations or analyses here considered are as follows:—

(*a*) **Zinc-Lead Ore (Sulphides).**
(*b*) **Arsenical Pyrites.**
(*c*) **Dolomite.**
(*d*) **Felspar.**
(*e*) **Fusible Metal.**
(*f*) **Babbit Metal.**
(*g*) **Smaltine.**
(*h*) **Chromite.**

(*a*) THE ANALYSIS OF A ZINC-LEAD SULPHIDE ORE.

The student must first analyse the ore qualitatively and will probably find that it contains some or all of the following (and perhaps additional)

elements or compounds—SiO_2, Pb, Cd, Cu, Fe, Al, Mn, Zn, S, and small quantities of **silver** and **gold**. The silver and gold will in most cases not be detected in the qualitative examination. *Aluminium* and *cadmium* may also not be present in appreciable quantity; or again, *manganese* or *copper* may be absent.

It is assumed here that all these elements are present, and, with the exception of silver and gold, are to be estimated. If the ore at the student's disposal contains fewer elements, the separations not required may be omitted, always taking care that any steps necessary to the succeeding estimation are not omitted.

The estimation of silver and gold is postponed to the section on Assaying.

Method, Reactions.—The ore is broken up by strong HNO_3 and HCl. A little H_2SO_4 is then added, which, along with that formed by oxidation of the sulphur, converts the lead into $PbSO_4$. The siliceous matter remains undissolved.

On filtering, SiO_2 and $PbSO_4$ are separated out. The $PbSO_4$ is dissolved and the Pb estimated volumetrically by the Molybdate method, the SiO_2 remaining being estimated gravimetrically.

From the filtrate, copper and cadmium are precipitated by H_2S. The joint sulphides are filtered off and dissolved in dilute hot HCl. The Cu is precipitated by aluminium and estimated by the Cyanide or Iodide method. The solution remaining after precipitation of the copper is titrated with $K_4FeC_6N_6$ to estimate the cadmium.

Manganese being present, the iron and alumina are precipitated by the Basic Acetate method, after conversion of the sulphates into chlorides by $BaCl_2$. The iron and alumina are estimated by a combination of gravimetric and volumetric methods.

The manganese is then precipitated by means of NH_4OH and bromine water.

The zinc which still remains in solution is then precipitated as the sulphide and estimated as oxide.

The sulphur in a fresh portion of the ore is oxidised by fuming HNO_3 and $KClO_3$ to H_2SO_4 and then estimated by precipitation as $BaSO_4$.

The following equations represent the chief reactions on which the methods depend :—

$$6PbS + 16HNO_3 = 6Pb(NO_3)_2 + \underline{3S_2} + 4NO + 8H_2O$$
$$2HNO_3 + S = H_2SO_4 + 2NO$$
$$Pb(NO_3)_2 + H_2SO_4 = \underline{PbSO_4} + 2HNO_3$$

The sulphur liberated forms globules which are slowly oxidised to H_2SO_4.

The zinc sulphide (blende) present is slowly soluble in acids excepting *aqua regia*, in which it is readily soluble.

$$HNO_3 + 3HCl = 2H_2O + NOCl + Cl_2$$
$$ZnS + Cl_2 = ZnCl_2 + S$$

the sulphur being oxidised as before to H_2SO_4.

The student may profitably fill in equations representing the solution of the copper, cadmium, iron, etc.

Sulphate of lead is soluble in ammonium acetate

$$2NH_4C_2H_3O_2 + PbSO_4 = Pb(C_2H_3O_2)_2 + (NH_4)_2SO_4$$

This equation seems somewhat doubtful. Perhaps the $PbSO_4$ is soluble

in the $NH_4C_2H_3O_2$ without the double decomposition. In the Molybdate titration

$$PbSO_4 + (NH_4)_2MoO_4 = (NH_4)_2SO_4 + PbMoO_4$$
$$or\ Pb(C_2H_3O_2)_2 + (NH_4)_2MoO_4 = 2NH_4C_2H_3O_2 + PbMoO_4$$

In the filtrate from the SiO_2 and $PbSO_4$

$$CuCl_2 + H_2S = CuS + 2HCl$$
$$CdCl_2 + H_2S = CdS + 2HCl$$

For the precipitation of CdS there must be no great excess of HCl present. With hot dilute HCl

$$CdS + 2HCl = CdCl_2 + H_2S\rightarrow$$
$$CuS + 2HCl = CuCl_2 + H_2S\rightarrow$$

$$and\ 3CuCl_2 + 2Al = 3Cu + 2AlCl_3$$

The reaction in the ferrocyanide volumetric estimation of the cadmium is similar to the one previously given for zinc.

Regarding the iron, alumina and manganese, the only equations that need be given here are as follows:—

$$Fe_2Cl_6 + 6NaC_2H_3O_2 = 2Fe(C_2H_3O_2)_3 + 6NaCl$$

On boiling, this ferric acetate breaks up into a basic acetate of rather uncertain composition.

$$Perhaps\ Fe(C_2H_3O_2)_3 + H_2O = Fe(C_2H_3O_2)_2OH + HC_2H_3O_2$$

Aluminium behaves somewhat similarly.

The manganese is then precipitated from an ammoniacal solution as the hydrated peroxide by means of bromine water.

For further details concerning these reactions the student is referred to the works of Menschutkin, Prescott, and Johnson, and Comey (*Dictionary of Solubilities*).

If, as often happens, the only determinations required are SiO_2, Pb, Zn and S the process may be cut down considerably, the SiO_2 and Pb being estimated in one portion, the zinc, by ferrocyanide, in another, and the sulphur in a third.

The Analysis.

SiO_2 and Pb.—Grind about 20 gms. of the ore to pass through an 80 sieve. Sample down to about 5 gms. and grind this sample in an agate mortar. Dry for 30 minutes in the oven at 110° C. Remove and weigh out 2 gms. of the ore.

Transfer to a beaker. Add 20 c.cs. 16E. HCl and 20 c.cs. 16E. HNO_3. Boil until the ore is completely decomposed. Transfer the contents of the beaker to a porcelain dish. Evaporate to dryness. Heat in the air oven at 160° C. for 15 minutes to render the SiO_2 insoluble. Moisten with 16E. HCl and add 10 c.cs. 5E. H_2SO_4. Heat on the hot plate till fumes of SO_3 come off. All the nitrates and chlorides are now changed to sulphates.

Cool and add about 50 c.cs. water. Filter and wash with E. H_2SO_4 till no reaction for iron is obtained (if iron be present). Remove the H_2SO_4 by alcohol, placing a fresh beaker under the funnel and washing till removed. The first filtrate is reserved and labelled, and contains Cu, Cd, Fe, Al, Mn, Zn (if present).

Dissolve out the $PbSO_4$ on the filter paper with $NH_4C_2H_3O_2$ as before directed (see Molybdate method), and estimate the Pb volumetrically by a standard solution of ammonium molybdate.

The filter paper and any siliceous matter thereon are now well washed with hot water, dried, incinerated, and weighed. This weight, less that of the filter ash, gives the SiO_2 present. Report the results as percentages of SiO_2 and Pb.

Cu and Cd.—To the 'reserved filtrate,' which should be about 150 c.cs. in volume, add 10 c.cs. 16E. HCl and pass H_2S till no further precipitate is obtained (test). The precipitate consists of CuS and CdS (if present). Filter and wash with H_2S water (made by passing H_2S into distilled water). Reserve the filtrate, which contains Fe, Al, Mn, Zn.

Dissolve the precipitated sulphides in hot 5E. HCl. Dilute to 50 c.cs. with water, and if copper is present precipitate with aluminium foil. Filter, wash, and titrate the filtrate with standard ferrocyanide as in the estimation of zinc. 1 c.c. $K_4FeC_6N_6 = x$ gms. Zn $x\frac{224}{230}$ = gms. Cd.

Estimate the copper by dissolving in HNO_3, adding NH_4 and titrating with standard KCN.

Note.—The more recent 'Phosphate' Method gives accurate results with cadmium.

Report the result as percentages of Cd and CN.

Fe and Al_2O_3.—The reserved filtrate from the H_2S precipitation is boiled until the H_2S is expelled (test by smell and by strips of filter paper dipped in lead acetate). Add 3 drops 16E. HNO_3 to oxidise any ferrous salts. As the solution contains H_2SO_4 and sulphates, these must be replaced by HCl and chlorides before precipitating the Fe and Al.

To the boiling solution add a boiling solution of E. $BaCl_2$ so long as any precipitate is formed. Filter and wash well the $BaSO_4$ precipitate. Neglect the precipitate. Reduce the filtrate by gentle boiling to about 150 c.cs. Carefully neutralise the solution by adding 5E. $(NH_4)_2CO_3$ drop by drop until a slight permanent precipitate just forms. Now add very cautiously, drop by drop, with stirring, E. HCl until the precipitate is *almost* redissolved, the solution now being slightly turbid.

Now add 10 c.cs. 5E. $NH_4C_2H_3O_2$ acidified with acetic acid. Boil for a few minutes and the basic acetates separate out. Let settle. Decant through a filter and transfer the precipitate to the filter, washing well with hot water. Dissolve the precipitate in HCl, neutralise and reprecipitate as before. Combine the filtrates.

Reserve the combined filtrate which contains the Mn and Zn. Under the funnel place a 100 c.c. flask and dissolve through the precipitate with 5E. HCl. Wash with a number of small washes of hot water, bringing the total filtrate nearly to 100 c.cs. Cool and make up to 100 c.cs. Mix well by shaking and transfer 50 c.cs. to a 200 c.c. beaker.

Boil the portion in the flask almost to dryness. Take up with 10 c.cs. E. HCl and 50 c.cs. water. In this solution estimate the iron by standard $K_2Cr_2O_7$. The result multiplied by two gives the total iron present in the ore taken; calculate the result in percentages of iron (Fe).

To the other 50 c.cs. in the beaker add NH_4HO to slight excess. Heat to boiling and boil for a few minutes. Let settle. Filter first by decantation and then on the paper. Wash till no reaction is obtained for chlorides. Dry the paper and precipitate in the air oven at 110° C. Ignite the paper separately from the precipitate. Weigh the ignited precipitate and paper. Deduct the weight of the filter ash and multiply the result obtained by two. This gives the total $Fe_2O_3 + Al_2O_3$ present, assuming that Fe and Al exist in the ore as oxides. The probability, however, is that the iron exists as a

sulphide, and the aluminium, of which only small quantities are present in such ores (if present at all), exists as Al_2O_3. To ascertain the percentage of Al_2O_3 present convert the percentage of Fe into terms of Fe_2O_3 by multiplying by $\frac{160}{112}$ or $\frac{10}{7}$. Deduct this result from the percentage of $Fe_2O_3 + Al_2O_3$, and the percentage of Al_2O_3 present is obtained.

Mn.—The combined filtrate from the double precipitation, as basic acetate, will be somewhat bulky, therefore it should be evaporated down to about 100 c.cs. Render neutral with NH_4HO and then add an excess of 10 c.cs. 5E. NH_4HO. Heat to boiling and add $\frac{E.}{2}$ Br solution till the precipitation of the hydrated peroxide of manganese is complete. The solution should now be distinctly yellow. Filter, reserving the filter, wash, dry, and incinerate, first with the bunsen and then with the blast, which converts the hydrated oxide into Mn_3O_4. Weigh. Deduct the filter ash and calculate the result as percentage of Mn.

The student may find it more convenient to estimate the Mn either in the ore or in the precipitate by Volhard's method, which see.

Zn.—Through the filtrate from the manganese pass H_2S till all the zinc is precipitated as ZnS. Filter. The zinc in this precipitate may be estimated by the Ferrocyanide method; or after washing, it may (the ZnS) be dissolved in a little 5E. HCl. Make up to 50 c.cs. Precipitate the zinc as carbonate by E. Na_2CO_3. Filter, wash, and ignite. The $ZnCO_3$ is changed to ZnO. Weigh as the oxide and calculate the percentage of Zn present.

S.—Powder about 1 gm. of the ore very finely in the agate mortar. Weigh out about ·5 gm. of this finely powdered ore. Mix on a large watch glass with about 2 gms. of finely powdered $KClO_3$. Transfer the mixture to a 200 c.c. flask. Add about 10 c.cs. strong *fuming* HNO_3, a little at a time, heating gently. Continue heating till any globules of sulphur that may have separated out are oxidised to sulphuric acid. Add about 1·0 gm. NaCl, which renders the H_2SO_4 non-volatile by converting it into Na_2SO_4.

Evaporate down to about 2 c.cs. Remove and, when nearly cool, dilute to about 50 c.cs., and add 3E. Na_2CO_3 in excess to precipitate the lead, iron, etc. The excess decomposes any $PbSO_4$ that may have formed during solution.

Boil for 30 to 40 minutes, adding water now and then to keep the volume nearly constant. Any $PbSO_4$ is now decomposed into $PbCO_3$.

Filter and wash till no reaction is obtained for H_2SO_4.

Acidify the filtrate cautiously with 5E. HCl. Boil to expel all CO_2, and precipitate as before with $BaCl_2$ solution.

From the weight of $BaSO_4$ calculate the percentage of S present.

Combining the Results.

Assuming that the ore was found to contain SiO_2, Pb, Cu, Cd, Fe, Al, Mn, Zn, and S, the results should be tabulated as follows:—

SiO_2	%
Pb	%
Cu	%
Cd	%
Fe	%
Al_2O_3	%
Mn	%
Zn	%
S	%
Total,	%

Where so many determinations have been made it is only by a rare chance that the results total to 100%; and if in the case given they range from 99% to 102% the work may be considered satisfactory, provided the difference be fairly distributed over the different estimations; but if, in duplicate, there is any serious discrepancy in any one estimation, that estimation must be repeated.

From the example just given the student will learn that a large amount of care, skill, and time is necessary in performing a complete analysis of a complex sulphide ore. Such an analysis will occupy a professional chemist for several days, and fortunately for him it does not often happen that complete analyses are required. In the case given, the chemist may be required to determine only **Pb**, **Zn**, and **S**, in which case, by using the Molybdate, Ferrocyanide, and the $KClO_3$ and fuming HNO_3 methods on three different portions from the same sample, good results may be quickly obtained.

(*b*) THE ANALYSIS OF ARSENICAL PYRITES.

Examine the ore qualitatively and ascertain what elements are present. It is assumed here that an ore is obtained which contains the following elements and compounds:—SiO_2, **Cu**, **As**, **Fe**, and **S**.

In this and the following analysis no special mention will be made of the necessary apparatus unless some particular kind or grouping of apparatus is required.

Method, Reactions.—This analysis is somewhat similar to that of the zinc-lead ore just given, and is inserted partly to give further practice on sulphide ores and partly to introduce some variations of methods.

One portion of the ore is taken for estimation of the arsenic by Dr Pearce's method.

Another portion is taken for estimation of the sulphur by the method previously given.

A third portion of the ore is taken for the estimation of the copper by the Iodide method, and a fourth portion is taken for the estimation of the silica and iron,—the former gravimetrically and the latter volumetrically.

Most of the reactions have already been explained, and any special precautions will be mentioned in the instructions.

The Analysis.

As.—As the ore examined is generally rich in arsenic there is danger of loss by volatilisation during the fusion, therefore to avoid such loss proceed as follows:—

Weigh out about ·25 gm. of the finely powdered and sampled ore. Transfer to a porcelain crucible, and drop by drop add about 3 c.cs. fuming nitric acid. This oxidises the arsenic and sulphur and prevents subsequent loss by volatilisation. Evaporate nearly to dryness, and add a slight excess of 5E. **NaHO**. Evaporate very carefully to dryness, and when dry and cool scrape out as much as possible into a small wedgewood mortar, and grind up with half the flux. Transfer the mixture back to the crucible. Place the other half of the flux in the mortar, and grind to pick up any remaining particles of the previous lot. Transfer to the crucible as a cover.

The fusion is now proceeded with as usual, and the arsenic is estimated by Dr Pearce's method as before described.

Calculate the result as percentage of arsenic (**As**).

S.—The sulphur is estimated as before on a ·5 gm. sample of the ore. The sulphur is oxidised to sulphuric acid, and the arsenic to arsenic acid. When the ore is thoroughly dissolved evaporate nearly to dryness. Take up with water to 50 c.cs. Neutralise with NH_4HO as in the arsenic estimation, and precipitate the arsenic acid as arsenate of silver. Filter and wash. To the filtrate add Na_2CO_3 in excess; this precipitates silver, iron, etc. Proceed with the remainder of the estimation as before, reporting the results as percentage of sulphur (**S**).

By this modified treatment any arseniate of potassium present is removed, and then the iron salts, thus leaving a solution containing but little that can interfere with the subsequent barium chloride precipitation.

Cu.—As the percentage of this element present in this ore is generally small, 2 to 5 gms. should be taken for this estimation.

Weigh out a suitable quantity of the ore, and decompose as instructed under the Iodide method, precipitating the copper with sheet aluminium. Observe the precaution of adding about 1 gm. $KClO_3$ crystals to oxidise any arsenic present to arsenic acid, otherwise a certain amount of iodine will be used up in the oxidation of the arsenious salts. Report the results as percentage of copper (**Cu**).

SiO_2 and **Fe.**—As the presence of arsenic frequently interferes with the estimation of iron, the usual method of estimation is somewhat modified, the Reduction method of Prof. L. J. W. Jones being here described.

Weigh out ·5 gm. of the finely powdered and sampled ore. Transfer to a casserole or porcelain dish. Add 10 c.cs. 16E. HNO_3. Heat till the ore is dissolved, and then evaporate almost to dryness. Add 5 c.cs. 16E. **HCl**, and repeat the evaporation. Take up with 10 c.cs. E. **HCl** and 40 c.cs. water.

Filter and wash well with hot water. Reserve the filtrate. Dry the filter and contents and incinerate (together). Deduct the weight of the ash after weighing, and report the result as percentage of siliceous matter (SiO_2).

To the filtrate add 20 gms. grain lead (assayer's test lead), and boil for five to ten minutes to reduce the iron (test).

$$Fe_2Cl_6 + Pb = 2FeCl_2 + PbCl_2$$

The iron is then determined by titration with standard potassium bichromate, and reported as percentage of iron (**Fe**).

Combine the results obtained and check by adding up the total, which should come within the limits of 99% to 101·5%. As a general rule, in complex analysis there is more likelihood of the total being over 100% than under. This is so for various reasons: The reagents generally contain some impurity which may increase the results; the vessels used are slightly soluble in the liquids contained therein, and this trace of dissolved glass, porcelain, or platinum (ferric chloride boiled in a platinum dish is reduced to ferrous chloride and platinum is dissolved) increases the results; a certain amount of dust from the atmosphere finds its way into the analysis, especially with long evaporations. Therefore of two totals, one 99·2% and the other 101%, the latter is more likely to be correct as far as manipulation and method are concerned. The student must not despair if his results are not too good at the outset. To obtain perfect results, that is, the best obtainable results, the qualitative analysis must identify *every* element present; the reagents must be perfectly pure, or valued by careful checking; the vessels used must be of the best quality, a liberal supply of platinum ware being necessary (more than the student can usually afford); the methods adopted must be chosen with due regard to the elements present, and the manipulation throughout must be of a high order. Such demands try the resources and time of the ex-

perienced and well trained chemist, and the student must remember that the task before him is arduous, and requires his very best attention and thought —he must be continually on guard to prevent the entrance of error, and to note any condition that may affect his results.

(*c*) THE ANALYSIS OF DOLOMITE.

Qualitative.—The substances that may be met with in a sample of dolomite are H_2O, CO_2, SiO_2, Al_2O_3, FeO (perhaps Fe_2O_3), CaO, MgO, and perhaps traces of one or more of the following, SrO, BaO, Na_2O, K_2O, MnO, ZnO, SO_3, and P_2O_5.

It will be assumed that the sample contains H_2O, CO_2, SiO_2, Al_2O_3, FeO, CaO, MgO. If other substances are present the student is referred to the works of Clowes and Coleman, Furman, Beringer, and especially to the work of Dr Hillebrand, *Bull. U.S. Geol. Survey*, No. 176 (published also in the *Chemical News*, 1901), much of the excellent material of which is, with slight modifications, of service in this and other mineral analyses.

Methods adopted.—A portion of the ore, which has been dried at 100° C., is heated in a hard glass tube and the evolved H_2O and CO_2 are collected and weighed in U tubes containing calcium chloride and soda-lime respectively.

Another portion of the dried ore is meanwhile dissolved in hydrochloric acid, evaporated to dryness, and taken up with hydrochloric acid and water. The SiO_2 (and silicates) is filtered off and estimated gravimetrically. (For special precautions, see "Silicates.")

In the filtrate the FeO and Al_2O_3 are estimated by precipitation with ammonia in the presence of ammonia chloride. The precipitate is dissolved and reprecipitated, the filtrates being combined. The FeO and Al_2O_3 are then estimated as before.

In the filtrate the CaO is precipitated as oxalate, washed, dissolved, reprecipitated, and then estimated volumetrically by standard $K_2Mn_2O_8$.

The magnesium in the filtrates from the Ca oxalate is then estimated by precipitation as $MgNH_4PO_4$, which, on incineration, changes to the pyrophosphate $Mg_2P_2O_7$.

The following equations show the chief reactions not previously considered.

On heating,
$$\left.\begin{matrix} CaCO_3 \\ MgCO_3 \\ FeCO_3 \end{matrix}\right\} = \left\{\begin{matrix} CaO \\ MgO \\ FeO \end{matrix}\right\} + \left\{\begin{matrix} CO_2 \\ CO_2 \\ CO_2 \end{matrix}\right\}$$

and
$$CO_2 + 2KHO = K_2CO_3 + H_2O$$
$$2H_2O + CaCl_2 = CaCl_2,2H_2O$$

The reactions on solution and on precipitation of the iron and alumina may be written out by the student. The calcium is precipitated as oxalate as follows,—

$$CaCl_2 + (NH_4)_2C_2O_4 = CaC_2O_4 + 2NH_4Cl$$

On ignition
$$CaC_2O_4 = CaO + CO_2 + CO$$

The magnesium is precipitated as a phosphate in concentrated solution thus—

$$MgCl_2 + Na_2HPO_4 = MgHPO_4 + 2NaCl$$

But in dilute solution with the further addition of ammonia,

$$MgCl_2 + Na_2HPO_4 + NH_4HO = MgNH_4PO_4 + 2NaCl + H_2O$$

Ammonium chloride must always be present to prevent the precipitation of magnesium hydroxide.

The Analysis.

H_2O and CO_2.—Thoroughly dry 4 or 5 gms. of the finely ground and sampled ore by heating for an hour at 100° in the oven.

Meanwhile prepare the apparatus previously used for the direct determination of water in copper sulphate, making the following alteration in the arrangement of the apparatus. Detach the guard tube on the left and replace it by a set of potash bulbs filled as directed in the Combustion of Coal (see Technical Analysis, Part III.).

If the set of bulbs is not provided with a guard tube, connect the previous guard tube to the free end of the bulbs. Attach another set of potash bulbs to the other end of the apparatus. Gently heat the ignition bulb and aspirate a current of air through the apparatus. Disconnect, close, and weigh the tube and bulbs. Reconnect and continue the heating and aspiration for about twenty minutes. Reweigh and repeat the operation till two successive weighings are constant within ·001 gm. Transfer 2 gms. of the dried ore to the ignition bulb. Connect up the apparatus and turn on the current of air. Heat *gently* at first, and in about ten minutes gradually raise the heat to a dull red. Continue the heating for another ten minutes, gradually raising the temperature to a bright red. Remove the burner and continue passing the air till cold. Remove the tubes, closing their ends with their respective rubber and glass rod caps. Weigh quickly. Calculate the results as percentages of H_2O and CO_2. Repeat the estimation on another 2 gms. of the ore.

Alternative Method for CO_2.—Weigh out about 1 gm. of the dried ore. Transfer to the flask *a* of a Schrötter CO_2 apparatus (fig.). Fill the gas washer *b* as shown with strong H_2SO_4. Fill the dropping funnel *c* about two-thirds full of 5E. H_2SO_4. See that all the stoppers are in place. Carefully wipe the apparatus with a dry linen cloth and weigh.

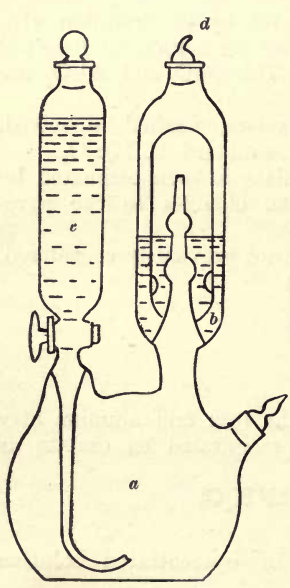


FIG. 72.

Now let the acid from the funnel gradually drop into the flask so that the CO_2 bubbles through *b* at about two bubbles per second. When the effervescence ceases, attach by a piece of rubber tubing an aspirator to *d*. Gently heat the flask over a small naked flame until the liquid just begins to boil, aspirating gently meanwhile. Remove from the heat. Remove the aspirator tube and close *d* with a small cap. When cool, reweigh. The difference in the two weights represents CO_2; the H_2O does not escape being absorbed (mostly) by the H_2SO_4. This method is both simple and speedy, and is satisfactory where no great accuracy is demanded, in which case the previous method or some modification of it is to be preferred.

Siliceous Matter (SiO_2 and Silicates).—Of the finely powdered ore, which has been dried at 100° C., weigh out about 1·5 gm. Transfer to a porcelain dish; cover with an inverted glass funnel. Cautiously add 5E. HCl by pouring it down the outside of the funnel. As soon as effervescence ceases remove the funnel, rinsing it into the dish. Carefully evaporate to dryness on the hot plate, placing a piece of sheet asbestos under the dish to prevent

boiling and spitting. Moisten the residue with 2 or 3 c.cs. 16E. HCl and gently warm. Add 50 c.cs. distilled water. Heat nearly to boiling and filter. Wash till free from chlorides. Reserve the filtrate. Dry the filter and precipitate. Incinerate together and weigh. Report the result, after deduction of filter ash, as percentage of siliceous matter.

FeO and Al_2O_3.—Oxidise the iron in the filtrate by adding 3 or 4 drops 16E. HNO_3 and heating to boiling. The iron and alumina are now to be precipitated by ammonia; but as $Al_2(HO)_6$ is slightly soluble in NH_4HO alone, but insoluble when NH_4Cl is present, this latter salt is added thus. In a small beaker mix 20 c.cs. 5E. HCl and 20 c.cs. 5E. NH_4HO, and add the mixture to the iron-alumina solution. 20E. NH_4HO is now added in *slight* excess and the mixture boiled for a few minutes. Filter and wash by decantation once or twice—not completely, as the precipitate is to be redissolved. Reserve the filtrate. Place a clean beaker under the funnel, and dissolve the precipitate through with hot 5E. HCl. Wash all traces of iron out of the paper, and in the solution reprecipitate the iron and alumina as before. Filter and wash till free from chlorides. Combine this filtrate with the filtrate from the first precipitation, and reserve the combined filtrate.

In the precipitate estimate the iron and alumina by dissolving in HCl, halving the solution, and in one half estimating the $Fe_2O_3 + Al_2O_3$ gravimetrically, and in the other half the Fe volumetrically.

The results are to be calculated as percentage of FeO and Al_2O_3. The calculations necessary are as follows:—Calculate the Fe in one half of the solution to Fe_2O_3. Subtract this quantity of Fe_2O_3 from the weight of Fe_2O_3,Al_2O_3 precipitate found in the other half of the solution. The difference represents the Al_2O_3 in half the weight of ore taken. Calculate the percentage of Al_2O_3 as usual. Calculate the Fe found in one half the solution to FeO. This represents the FeO in one half the weight of ore taken. Calculate the percentage as usual.

In reporting the results of an analysis, each element should be calculated to the form in which it exists in the rock, ore, or other matter analysed. Regarding the condition of the iron in a carbonate ore some doubt exists. It may exist as $FeCO_3$ or as $FeCO_3 + Fe_2O_3$; in the former case it is reported as FeO (CO_2 being separately estimated); in the latter case partly as FeO and partly as Fe_2O_3, requiring separate determinations of ferrous and ferric compounds (see Analysis of Silicates, Hillebrand). For the present—though not strictly accurate—the student may report the iron as FeO.

Ca.—The combined filtrates from the double precipitation of iron and alumina being somewhat bulky, are evaporated down to about 150 c.cs. See that, if required, sufficient ammonia is added to make the liquid smell distinctly of that reagent. The calcium is now precipitated as oxalate by the addition of excess (about one quarter more than is necessary to precipitate all the calcium present) of E. $(NH_4)_2C_2O_4$. This excess largely prevents the precipitation of magnesium oxalate.

Boil for a few minutes and filter, washing once or twice with hot water by decantation. Place the precipitation beaker under the funnel, and dissolve through the precipitate with hot 5E. HCl, washing till free from chlorides. Render the solution alkaline with NH_4HO as before, and reprecipitate the calcium as oxalate. Any traces of MgC_2O_4 are removed by this double precipitation.

Wash well, and combine the filtrates from the two precipitations. Reserve the combined filtrate.

The calcium in the precipitate may now be estimated volumetrically by

solution in sulphuric acid and titration with standard potassium permanganate. Report the result as percentage of calcium oxide (CaO).

Mg.—Concentrate the combined filtrates from the calcium precipitate to about 150 c.cs. by gently boiling in a beaker. Transfer to a porcelain evaporating basin and evaporate to dryness, and then cautiously heated over a naked bunsen to expel the ammonia salts. When cool, dissolve the residue in 5E. HCl (about 20 c.cs.). Heat and filter through a small paper, washing out the dish and then the paper with hot water, and bringing the filtrate up to about 150 c.cs.

When cold (cool under the tap), carefully add about 40 c.cs. E. Na_2HPO_4. After adding the phosphate, stir with a glass rod (preferably of thin glass tube, closed and grounded at one end), and avoid touching the sides of the beaker with the rod, or the crystals of $MgNH_4PO_4$ will adhere firmly to the beaker, and cause subsequent trouble. Cold and frequent agitation assist the precipitation, and if convenient the beaker may be set in a dish of iced water or in an ice chest. Allow to stand for six to twelve hours to complete the precipitation. After standing, test if the precipitation is complete or not by removing about ·5 c.c. in a test tube, and adding about ·5 c.c. magnesia mixture (made by dissolving 1 gm. $MgSO_4$ and 1 gm. NH_4Cl in 8 c.cs. H_2O, and adding 3 c.cs. 20 E. NH_4HO. If a precipitate forms, it shows that sufficient Na_2HPO_4 has been added to the liquid; but if no precipitate forms, add 10 c.cs. more of the E. Na_2HPO_4. Stir and let stand a few hours.

When precipitation is complete, filter. Wash with dilute NH_4HO (1 part 20 E. NH_4HO to 3 parts H_2O) till no reaction is obtained for chlorides (acidify a few drops of the washings with pure HNO_3 and test with $AgNO_3$). Dry the filter and precipitate. Transfer the precipitate to a crucible (preferably platinum), and incinerate the filter on a platinum wire. If, as sometimes happens, difficulty is met with in incinerating the paper, it should, before ignition, be moistened with 5 E. NH_4NO_3 solution, dried, and then incinerated.

Transfer the filter ash to the crucible, and heat it and the contents cautiously with a bunsen, using a small flame. When no more ammonia fumes (detect by smell or acid on a glass rod) come off, raise the heat to a dull red for ten minutes, and then heat to a bright red over the blast for another ten minutes. Remove in the desiccator, cool and weigh. Repeat the ignition under the blast till the weight is constant within the required limits. If the precipitate is discoloured or black, moisten with a drop or two of strong HNO_3 and re-ignite.

After deduction of the ash, calculate from the weight of $Mg_2P_2O_7$ the percentage of magnesium oxide in the mineral.

Summarise the combined results, adding up the percentages of H_2O, CO_2, SiO_2, FeO, Al_2O_3, CaO, and MgO. Run a duplicate, repeating any doubtful estimations, and check the total results.

(*d*) THE ANALYSIS (partial) OF AN INSOLUBLE SILICATE.

For analysis the student may procure a sample of a felspar such as 'orthoclase,' or a sample of one of the more common igneous rocks such as granite or syenite.

The complete analysis of a rock involves the determination of approximately ten to twenty-five components as follows:—SiO_2, Al_2O, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O, H_2O, and small quantities of certain of the following—TiO_2, ZrO_2, P_2O_5, CO_2, SO_3, Cl, S, C, Cr_2O_3, V_2O_3, NiO, CoO, CuO, MnO, SrO, BaO, Li_2O.

It is only intended here to present instructions for a partial analysis of a complex silicate, as the complete analysis is beyond the student's present capabilities, and should not be attempted till the end of his third year. As

a partial analysis, though accurately conducted, cannot represent the true composition of the silicate, some brief notes will be added, after summarising the methods used, indicating where error will probably occur, and what may be the extent of such error. When the degree and probability of error are approximately known, the partial analysis becomes to a certain extent reliable; but if the analysis is required for exacting mineralogical or petrological work, a partial analysis is of no great value, and must be replaced by a complete analysis based on the lines laid down by Dr Hillebrand in his paper entitled "Some Principles and Methods of Rock Analysis," and published as Bulletin No. 176, U.S. Geol. Survey. With the purest reagents, a liberal supply of platinum vessels, a clean laboratory, and proper facilities for working, he requires that the results of a complete analysis when summed up shall range between 99·75 and 100·50. The student who wishes an ideal of high-class analytical work is strongly advised to refer to the bulletin mentioned. The high degree of accuracy therein demanded can be obtained only by continued practice and a thorough knowledge of theoretical chemistry, more especially as applied to the properties (chiefly the solubility) of the various components of the rock or other silicate, and of the precipitates obtained in the analysis.

Method of Analysis.—In the partial analysis the following components will be estimated, subject to the errors to be mentioned :—SiO_2, Al_2O_3, Fe_2O_3, FeO, CaO, MgO, Na_2O, K_2O, and H_2O.

The *moisture* (hygroscopic) is first estimated by drying a weighed quantity of the finely ground ore at 110° C. Then the powder is ignited at a red heat, and the result reported as "*loss on ignition*" (chiefly combined water). The powder is then fused with Na_2CO_3, or Na_2CO_3,K_2CO_3, and the fused mass dissolved in dilute HCl, evaporated to dryness, taken up with dilute HCl, the SiO_2 filtered off and estimated gravimetrically.

In the solution the Al_2O_3, Fe as Fe_2O_3, CaO, and MgO are estimated as usual.

The FeO is estimated by dissolving a fresh portion of the powder in HF and dilute H_2SO_4 in an atmosphere of CO_2, and titrating direct with $K_2Mn_2O_8$, the ferrous iron alone being estimated by this method.

The Na_2O and K_2O are separated from their silicates (J. Lawrence Smith's method), heating to a red heat a mixture of one part rock, three parts $CaCO_3$, and one half part NH_4Cl. On digesting the mass in hot water the solution contains $CaCl_2$, NaCl, KCl, and $Ca(OH)_2$. The lime and magnesia are separated, and the joint chlorides are then estimated, after which they are dissolved, and the potassium precipitated as K_2PtCl_6, and from this the K_2O is calculated. Na_2O is then estimated by difference, the calculation being given later on.

Probable Errors.—The ignition loss should not be reported as H_2O. It will include any CO_2 and SO_2. Also any trace of FeS_2 present will be oxidised to Fe_2O_3, thereby introducing slight error.

Again, if the TiO_2 be not separately estimated, part of it is included with the SiO_2, and most of it with the Al_2O_3. The TiO_2 may amount to 2% or 3%, though on the average it is, along with P_2O_5, about ·8% (as estimated by Prof. F. W. Clarke). Also any P_2O_5 is estimated along with the Al_2O_3. Therefore the Al_2O_3 may be overestimated by 2 or 3%; on the average, ·8%.

Further, BaO and SrO are nearly always present, and to the extent sometimes of over 1%, the error falling on the CaO and MgO.

Other errors due to the non-estimation of SO_3, Cl, MnO, etc., will also occur, though these errors are, as a rule, not so serious as those first mentioned.

Briefly, with a summation of results between 99·5 and 101, there may be an error of several per cent. even in single estimations.

Of course the true value of the error cannot be determined without further

analyses, therefore the student must accept the results obtained with the more or less vague qualifications stated.

The Analysis.—The first step in the analysis is the preparation of the sample, which is obtained in the usual manner. A sample of about 10 gms. is then reduced in a large diamond mortar. About 5 gms. of the coarse powder is sampled, and then ground to an impalpable powder in a large agate mortar (10 cm. diameter is a convenient size). About ·25 gm. at a time is transferred to the agate and ground till, on rubbing a little of the powder between the tips of the fingers, not the least grit is felt, and it rubs off smoothly and impalpably. This process is tedious, but an extra half-hour here will save subsequent trouble on fusion and other operations.

Moisture (Hygroscopic).—Weigh out 1 gm. of the finely powdered silicate as follows :—Counterbalance with the weights a large *platinum* crucible (25 c.cs. or more). Place an additional 1 gm. weight on the pan with the weights, then proceed to add to the crucible approximately 1 gm. of the powder, either adjusting to the exact weight or weighing exactly with the rider (the latter saves time). At the same time weigh out two lots of ·5 gm. and 1 gm. respectively. Transfer to watch glasses, cover with funnels, and reserve for the determination of the alkalies and ferrous iron.

Transfer the platinum crucible and contents to the oven at 110° C. Heat for one hour. Remove, cool, and weigh. Reheat for fifteen minutes. Again weigh, and repeat the heating till constant to the usual limits. Report the resulting difference in weight as percentage of moisture.

Ignition Loss.—Transfer the crucible to a suitable triangle (either platinum wire or pipeclay wrapped in platinum foil) on a tripod. Ignite for fifteen minutes over the bunsen at a red heat, and then for ten minutes over the blast. Remove as usual. Cool and weigh. Blast again for another ten minutes. Again weigh, and repeat till constant as required. Report the difference caused by this operation as percentage of "Ignition Loss" (mostly combined water).

SiO_2.—Transfer the contents of the crucible to a small glass mortar. Add 6 gms. pure anhydrous Na_2CO_3 (Merck's guaranteed), and mix thoroughly and very intimately by grinding with the pestle. Transfer the mixture to the crucible, which is then placed on the triangle, and the lid placed on at an angle, so that the contents will be visible during fusion. The Na_2CO_3 used should be afterwards checked by running a blank fusion on the carbonate alone, and estimating the SiO_2, Al_2O_3, and CaO in the flux.

Proceed at first to heat the crucible with a bunsen, and when it shows signs of melting round the edges apply the blast, directing the flame at an angle against the side and bottom. Regulate the blast so that the charge does not boil over. Continue heating till the contents of the crucible are in a state of quiet fusion, the charge having subsided into a clear liquid at the bottom of the crucible. Remove the flame, and when nearly solidifying, grasp the triangle in the forceps and give the crucible a gentle motion to swirl the contents up the sides. Continue the motion till the mass solidifies. A bluish green coloured mass indicates manganese, which however may be present even when this indication is absent.

Transfer the crucible and lid to a 15 cm. porcelain evaporating dish. Cover with an inverted glass funnel. Dissolve the melt by pouring down outer edge of the funnel excess of 5E. HCl. When the mass seems completely detached from the crucible, rinse the funnel into the dish, and remove the crucible and lid with the aid of a glass rod. The crucible is raised up the side of the basin, washed well outside with hot water, then taken in the fingers and the interior rinsed out; the lid is treated similarly. If the

fusion has been complete there should be no gritty particles at the bottom of the dish.

The SiO_2 in solution must now be separated by evaporation. According to Dr Hillebrand this is best done as follows. Evaporate the solution till almost dry. Break up the gelatinous mass with a glass or platinum rod to facilitate drying, and continue till just dry. Take up with about 100 c.cs. E. HCl. Filter and wash with hot water till free from chlorides. Reserve the precipitate and evaporate the filtrate to dryness in an evaporating dish. Again take up with 100 c.cs. E. HCl. Filter and wash as before. The remainder of the SiO_2 is thus separated out. Reserve the filtrate.

Dry the two filters and precipitates and ignite them in a weighed platinum crucible, first at a dull red, and then for about twenty minutes over the blast. As a check, weigh the empty crucible after the last weighing, and note any change in the weight of the crucible.

As a further check, transfer the precipitate back to the crucible. Add about 10 c.cs. strong HF and 3 or 4 drops 36E. H_2SO_4. (The HF can be obtained pure in ceresine bottles; if impure, a blank must be run for residue.) Evaporate in a fume cupboard and add fresh portions of HF as the evaporation goes on. Evaporate to dryness. Ignite and weigh. Repeat the process till constant. The loss in weight is SiO_2.

For the present the student may report the total percentage of SiO_2 and residue, that is, the weight of the first precipitate as SiO_2, etc.

$Al_2O_3(Fe_2O_3)$, etc.—The joint Al_2O_3,Fe_2O_3 precipitate will be determined as usual, and the Al_2O_3 estimated by difference, throwing the burden of error on the alumina.

If manganese is present precipitate the iron and alumina by the Basic Acetate method, but, if absent, by the Ammonia precipitation.

To the filtrate from the SiO_2, NH_4HO and NH_4Cl are added as usual to precipitate the iron and alumina. The precipitate is filtered off, dissolved and reprecipitated. Combine the filtrates and reserve the combined filtrate.

Dry the precipitate and ignite separately the filter and precipitate. Combine and blast for five or ten minutes. Weigh and repeat till constant. The iron present is now determined as follows:—To the precipitate in the platinum crucible add about 5 gms. $KHSO_4$ and fuse gently over a good rose-bunsen for 2 to 4 hours. When the precipitate is dissolved, remove and swirl the mass when cooling. Take up the melt in a 200 c.c. beaker with about 100 c.cs. hot E. H_2SO_4. When dissolved, filter and wash well. Reduce the filtrate by a brisk current of H_2S, heating to boiling meanwhile. Whilst this is going on fit up a 'Kipp' to generate CO_2, and lead its delivery tube into a flask which is to be set under a funnel to catch the filtrate from the H_2S solution. Continue passing H_2S for a short time after boiling. Filter quickly into the flask, washing quickly. Remove the flask and 'Kipp' (still passing CO_2), and heat the flask to boiling to expel H_2S. When expelled, cool under the tap (still passing CO_2) and when cool titrate with $K_2Mn_2O_8$. Calculate the result to Fe_2O_3. From this will have to be subtracted the quantity of Fe_2O_3 equivalent to the ferrous iron (FeO) in the portion analysed (see following). The difference is the Fe_2O_3 present. The Al_2O_3, etc. is calculated by deducting the total Fe_2O_3 (from the titration) from the weight of the joint oxide precipitate. Report the result as percentage of Al_2O_3, etc.

The Fe_2O_3 cannot be reported until the FeO determination has been made.

CaO, etc., MgO, etc.—In the following precipitation a small quantity of SrO and traces of BaO will probably be estimated with the CaO.

Evaporate the combined filtrate from the iron and alumina precipitation to dryness and heat to expel the excess of ammonia salts. Take up the residue with about 20 c.cs. E. HCl and 100 c.cs. water. Filter if necessary, and estimate the calcium as instructed in the analysis of dolomite, precipitating twice and reserving the filtrate for the estimation of the magnesium. Report the result in percentage of CaO, etc.

The magnesium in the filtrate is then estimated as before by precipitation with Na_2HPO_4, and the result reported as percentage of MgO, etc. Hillebrand recommends that the phosphate solution ($NaNH_4HPO_4$) should be added to the *acid* solution of magnesium, and that then NH_4HO should be added in *slight* excess. To facilitate the ignition he recommends Mastbaum's method of applying the full flame to the precipitate wrapped in its paper (in the crucible), and when most of the carbon is burned off the mass is moistened with 3 or 4 drops of 16E. HNO_3, evaporated carefully, heated with the full burner for a few minutes and then with the blast for half a minute.

FeO.—Transfer the 1 gm. portion (previously reserved) of powder to a large *platinum* crucible, moisten with 36E. H_2SO_4, and place in a suitable sized hole on the water bath. Arrange a 'Kipp' to deliver CO_2. Round the crucible place a cylinder of tin about 8 cm. high, and open at both ends. Lead the CO_2 delivery tube to within 2 cm. of the top of the crucible. Raise the cylinder. Pour into the crucible about 20 c.cs. HF. Enclose with the cylinder. Pass a steady stream of CO_2. Heat the water in the bath, and lightly cover the top of the cylinder with a small piece of lead foil. When boiling commences the gas current may be slackened. Continue the heating for about 40 minutes. Remove the flame, and cool the crucible by quickly transferring the crucible and fittings to a porcelain basin containing a little cold water.

When cool, empty the contents of the crucible into a 200 c.c. beaker containing 50 c.cs. water. Wash out the crucible, and titrate the solution with standard $K_2Mn_2O_8$. Calculate the result to FeO, and report as percentage of FeO.

Calculate the percentage of FeO to Fe_2O_3, and deduct from the percentage of Fe_2O_3 previously found, and the result is the percentage of Fe_2O_3 in the rock.

Na_2O, K_2O.—The third portion of the finely ground rock is now taken and carefully and intimately ground with ·5 gm. pure NH_4Cl (prepared by neutralising pure HCl with NH_4HO, evaporating to dryness and recrystallizing). When thoroughly mixed, add 4 gms. pure $CaCO_3$ (prepared by dissolving and precipitating the $CaCO_3$ from pure crystalline calcite). Continue grinding till a thorough mixture is obtained. Transfer to a covered platinum crucible (20 to 30 c.c.).

Through a piece of asbestos board cut a hole so that the crucible will project down through it by about two-fifths its length. Set on a tripod, and under it bring a quadruple bunsen burner. Heat at first with a low flame about 3 cm. away from the crucible, and as soon as an odour of ammonia ceases increase the heat so that the bottom of the crucible is at a dull red heat. Continue at this temperature for 50 minutes.

Remove the crucible lid and contents. Detach the sintered cake into a 100 c.c. beaker, softening the mass with water if necessary. Wash out the crucible and lid with a little hot water. Heat on the hot plate, breaking up any lumps with a glass rod. Filter and wash by decantation till free from chlorides. (The residue should completely dissolve on testing with excess of HCl.)

Heat the filtrate to boiling, and precipitate the lime with NH_4HO and $(NH_4)_2CO_3$, adding 2 drops 5E, $BaCl_2$ to precipitate any sulphates. Filter and wash well. Evaporate the filtrate to about 100 c.cs.; precipitate any traces of lime left with NH_4HO and $(NH_4)_2CO_3$. Evaporate the filtrate to dryness in (preferably) a platinum dish, and carefully drive off the ammonia salts. Dissolve the residue in about 5 c.cs. distilled water, and add a slight excess of NH_4HO and $(NH_4)_2C_2O_4$ to precipitate any traces of lime still remaining. Filter through a 5 cm. paper in a small funnel, and catch the filtrate in a small weighted platinum dish (or porcelain crucible). Wash with hot water till free from chlorides.

Evaporate the filtrate to dryness. Gently ignite. Cool and moisten with 5E. HCl to decompose any alkaline carbonates. Ignite and weigh, and note the result as weight of joint chlorides (NaCl,KCl).

Dissolve the joint chlorides in about 5 c.cs. water. Transfer, if necessary, to a porcelain crucible, washing out the platinum dish several times with a little hot water. Add two drops 5E. HCl and a slight excess of 5E. $PtCl_4$ solution (the liquid should on evaporation be yellow and remain yellow). Evaporate on the water bath till semi-solid (solidifies on cooling).

Add about 10 c.cs. absolute alcohol. Stir with a small glass rod. Let settle, and decant through a very small filter. Wash by alcohol three or four times, keeping as much of the precipitate as possible off the paper. Dry the filter dish and contents. Transfer the contents of the dish to a weighed crucible or dish, and wash through the precipitate on the paper with hot water. Evaporate the contents of the crucible to dryness, and then heat to 135° C. in an air bath, and when cold weigh as K_2PtCl_6.

Calculate the result to KCl $\left(\text{multiply by } \frac{2KCl}{K_2PtCl_6} = \frac{149}{486} = \cdot 307\right)$. Subtract the result from the joint chlorides, and the difference is the NaCl.

Convert the NaCl and KCl to Na_2O and K_2O, and the result is the Na_2O and K_2O in ·5 gm. rock. Calculate the percentage as usual, reporting as percentage Na_2O, etc. (includes Li_2O) and percentage K_2O.

Summarising Results. — The results obtained may be stated in the following form:—

H_2O (hygroscopic)	
Ignition loss (H_2O, CO_2, etc.)	
SiO_2, etc.	
Al_2O_3, etc.	
Fe_2O_3,	
FeO	
MgO, etc.	
CaO, etc.	
Na_2O, etc.	
K_2O	
Total	

The results so stated, though only partial, are of value in that they show the conditions of analysis, and are in no way misleading to other chemists. The analysis as presented is lengthy, yet not so lengthy by far as a complete analysis would be. The student must run duplicates of all estimations, and must again repeat unsatisfactory determinations. Unfortunately the time at the disposal of many metallurgical students is so brief that full justice is not done to an analysis of this kind. Rather than

attempt the analysis as set down, and not carry through duplicates, the student should confine his attention to part of the analysis, omitting, say, **FeO** and Na_2O,K_2O determinations, his results being submitted to the demonstrator, who has carefully analysed the sample examined. Or again the student may confine his attention to the estimation of SiO_2, etc., K_2O, Na_2O, etc. A few components correctly estimated are of more value than twenty to thirty careless estimations, even if by mere chance the summation of results comes within the desired limits. Much of the detail of this analysis is given as laid down by Dr Hillebrand, and after following the details given the student will be able to appreciate more fully the article referred to. The elaborate precautions therein taken to secure accuracy serve to give the student an ideal which should go far to counteract the tendency to carelessness in the student reared exclusively on technical analysis, where a certain amount of accuracy is sacrificed to speed. Both types of analysis have their particular place, and the metallurgical student must be capable of undertaking either class of work as occasion may demand, the object of the analysis being the chief guide as to the class of work adopted.

(*e*) THE ANALYSIS OF FUSIBLE METAL.

Fusible metal is an alloy, the chief constituents of which are *tin*, *lead*, *bismuth*, *cadmium*, and traces of other metals. The instructions given detail the methods of estimating the four metals mentioned.

Method, Reactions, etc.—Various methods for the analysis of alloys of this nature will be found on reference to the more advanced text-books which the student may consult with advantage (Stillman, Furman, Phillips, etc.). The methods here adopted are as follows, it being assumed that a qualitative analysis has preceded the quantitative.

The alloy is dissolved in aqua regia, and excess of acid expelled. After dilution excess of **NaHO** and Na_2S are added. The metals are precipitated as sulphides and the tin sulphide is redissolved. Filter and precipitate the tin by acidifying the filtrate with **HCl**. The precipitate is incinerated and weighed as oxide.

The precipitate of sulphides of bismuth, lead, and cadmium is dissolved in nitric acid and the lead precipitated as sulphate. The bismuth is estimated in the filtrate by precipitation as oxychloride, re-solution in acid, followed by precipitation with ammonium carbonate, and weighing as the oxide.

The cadmium is then estimated in the filtrate from the bismuth by precipitation with sulphuretted hydrogen. The precipitate is dissolved in **HCl** and titrated with standard potassium ferrocyanide. As an alternative the Phosphate Method may be used.

The Analysis.

Sn.—Weigh out 1 gm. of drillings or turnings of the alloy. Transfer to a 200 c.c. conical beaker and add about 20 c.cs. aqua regia. Heat on the plate till the excess of acid is expelled. Dilute to about 50 c.cs. A certain amount of the white oxychloride of bismuth will be formed. Add 5E. **NaHO** in excess, and then add 5E. Na_2S in excess. (This Na_2S solution should be saturated with H_2S.) Allow to stand in a warm place for three or four hours. Filter and wash with E. Na_2S (till free from chlorides). Reserve the precipitate.

Evaporate the filtrate to about 100 c.cs. and acidify with 5E. **HCl**. Let stand about two hours. Filter, wash, dry, ignite, filter and precipitate

(separately), heating cautiously at first, and then more strongly till the sulphide is completely converted into oxide. Add about ·25 gm. *pure* $(NH_4)_2CO_3$ to completely eliminate any sulphate formed during incineration (see the "Chemical Reactions of the Roasting Process," *Assaying*, Part III.). Continue heating and adding fresh portions of $(NH_4)_2CO_3$. Three or four additions will suffice to bring the weight constant. After deducting the ash calculate, from the weight of SnO_2 found, the percentage of **Sn** present.

Pb.—The combined precipitate of bismuth, lead, and cadmium is dissolved in 5E. HNO_3; 10 c.cs. 5E. **HCl** are added, and the solution evaporated almost to dryness. Take up with about 40 c.cs. water, adding 16E. **HCl** sufficient to prevent the formation of bismuth oxychloride. Add excess of 5E. H_2SO_4 and about 30 c.cs. of absolute alcohol (or rectified spirit). Allow the precipitate to settle.

Filter, wash with alcohol, and estimate the $PbSO_4$ gravimetrically as previously instructed. From the weight of $PbSO_4$ calculate the percentage of **Pb** present.

Note.—This precipitate should be examined qualitatively for traces of bismuth or other metals. This remark applies also to the tin and other precipitates obtained in this analysis.

Bi.—Boil off the alcohol from the filtrate from the $PbSO_4$ precipitate. Dilute largely with water to precipitate the bismuth as oxychloride. (Test the completeness of the precipitation by filtering a small portion and diluting further.) Filter off the oxychloride, washing well. Dissolve the oxychloride in 5E. HNO_3. Add NH_4HO till just alkaline, and then excess of E. $(NH_4)_2CO_3$. Heat to boiling, and allow to stand till the bismuth carbonate settles. Filter and wash. Dry and incinerate the paper separately, finally igniting filter ash and carbonate together in a small *porcelain* crucible at a dull red heat. Weigh as Bi_2O_3, and calculate the percentage of **Bi** present.

Cd.—Concentrate by evaporation the filtrate from the oxychloride precipitation to about 100 c.cs. In this precipitation by H_2S there must be only a very small quantity of hydrochloric acid present. The quantity of acid present should be regulated by neutralising with NH_4HO and then adding a *slight* excess of **HCl**.

Through the solution pass a brisk current of H_2S (warming the solution) till a precipitate ceases to form. Filter off the precipitated sulphide. Wash with H_2S water. Dissolve the precipitate in hot 5E. **HCl**. Dilute to about 150 c.cs.

The solution is now ready for titration with standard $K_4FeC_6N_6$ solution. The details of this operation and the necessary calculations have been previously given. Calculate the percentage of cadmium (**Cd**) present.

Note.—If traces of other metals are present, they may, if time permits, be estimated, proportionately large samples being taken for analysis. If such elements are not estimated, the summation of results will, if the work be correct, come short of 100·00.

(*f*) THE ANALYSIS OF BABBITT METAL.

This alloy consists of *tin*, *antimony*, *lead*, and a little *copper*. On reference to Stillman's *Engineering Chemistry*, the student will find two methods of analysis given—that of E. M. Bruce and that of G. W. Thompson. Bruce's method, as modified by Stillman, is here given, but the student is advised to refer to the work quoted and read the description of Thompson's method, which is also suitable for fusible metal. The same work gives a scheme of

analysis for white metal containing Sb, Sn, Pb, Cu, Bi, Fe, Al, Zn. This scheme will be of service to the student for reference if he meets with other combinations of elements than those here given.

Method of Analysis.

The alloy is dissolved in nitric acid, the free acid expelled and the concentrated liquid neutralised with NaHO and excess of Na_2S added. On gently boiling for some time the precipitate consists of the sulphides of lead and copper, and the solution contains the sulphides of tin and antimony. On filtering, the Na_2S in the filtrate is decomposed by $H_2C_2O_4$, the solution boiled, H_2S passed. The precipitate of Sb_2S_3 and S is filtered off; the S removed with CS_2 and the Sb_2S_3 weighed. The filtrate from the Sb_2S_3 is boiled with H_2SO_4 to decompose the $H_2C_2O_4$. Then, on dilution, H_2S is passed, sulphide of tin precipitated, collected, incinerated, and weighed as SnO_2.

The copper and lead sulphide is dissolved in HNO_3, the lead estimated as sulphate gravimetrically or volumetrically, and the copper remaining in the solution is precipitated as the sulphide (or metal), dissolved, and estimated volumetrically.

The Analysis.

Sb.—Weigh out 2 gms. (Stillman recommends 5 gms., which seems excessive) of the drillings of the alloy. Transfer to a 150 c.c. beaker (conical). Add 20 c.cs. 5E. HNO_3, and heat till decomposition is complete and nearly all the free acid is evaporated. When about 5 c.cs. of the solution remain add 15 c.cs. water and then 5E. NaHO till nearly neutral. Then add 30 c.cs. 5E. Na_2S solution (saturated with H_2S). Stir well the mixture and boil gently for half an hour. Filter on a 9 cm. paper and wash well with $\frac{1}{20}$E. Na_2S. Reserve the precipitate (lead and copper sulphides).

Dilute the filtrate to 200 c.cs. and boil. Cautiously add finely powdered pure oxalic acid till the Na_2S is all decomposed and a milky separation appears mixed with a precipitate, which at first appears black. Boil for twenty minutes. Pass H_2S for ten minutes. Filter through a Gooch crucible and wash with hot water. The precipitate consists of $Sb_2S_3 + S$. Wash with alcohol, then with pure carbon disulphide, and then with alcohol. Dry and weigh, and repeat the washing and weighing till constant.

From the weight of Sb_2S_3 found calculate the percentage of antimony (Sb) present.

Sn.—To the filtrate from the Sb_2S_3 (neglecting of course the C_2H_5OH and CS_2 washings) add 30 c.cs. 36E. H_2SO_4 and boil down till all the oxalic acid is decomposed and copious white fumes of SO_3 come off. Cool. Dilute carefully to 200 c.cs. Mix well and filter quickly. Dilute the filtrate to 300 c.cs. Warm and pass H_2S till the precipitation of the tin is complete. Filter and wash well with hot water. Dry, ignite, and weigh as SnO_2, and from the weight of SnO_2 found calculate the percentage of tin (Sn) present.

Pb.—The reserved precipitate containing copper and lead sulphides is dissolved in nitric acid, and the lead is precipitated as sulphate by sulphuric acid, filtered on a Gooch crucible, washed with dilute H_2SO_4 (5% approximately E.), dried, and ignited over a bunsen burner. The precipitate is then weighed, and the percentage of lead (Pb) calculated as usual.

Cu.—The filtrate from the lead precipitate contains the copper, which

may be precipitated by H_2S and dissolved and estimated volumetrically, the results being reported as percentage of copper.

Note.—Antimony and tin may be separated by fusing their oxides with pure NaOH in a silver crucible, when antimoniate and stannate of sodium are formed, the former being insoluble and the latter soluble in water. (See Stillman, p. 301.)

(*g*) THE ANALYSIS OF SMALTINE.

The composition of this mineral is given by Dana (*Text-Book of Mineralogy*) as very variable, and for the typical kind he gives the formula $(CoFeNi)As_2$, but in the analysis of different varieties the arsenic ranges from about 60% to 74%; the cobalt from 2% to 15%; the nickel from 2% to 15%; the iron from 1% to 12%; with sometimes a few per cent. of sulphur and copper.

For detailed analysis of minerals the student is referred to Dana's *System of Mineralogy*, and for analysis of rocks to the works of Rosenbusch, more especially *Elemente der Gesteinlehre.*

The tabulated results of rock analysis in the last mentioned work, though in German, will be quite intelligible, even to the student whose knowledge of that language is small.

Conduct as usual a careful qualitative examination of the mineral. From the results of the qualitative examination the student should now be able to form some idea as to the quantity of each element found.

It will be assumed here that the elements found are As, Fe, Ni, and Co. If other elements such as Cu, S, etc. are found, the scheme must be altered to include their estimation (consult Menschutkin and Furman). SiO_2 may be present, mixed with the mineral.

Method adopted.—The arsenic is determined as usual by Dr Pearce's method.

A fresh portion of the ore is broken up with acid; the arsenic and other elements of that group are precipitated by sulphuretted hydrogen. The iron in the filtrate is precipitated as basic acetate, and then dissolved and estimated volumetrically. In the filtrate from the iron the nickel and cobalt are precipitated together in the metallic state and weighed as the metals. The precipitated metals are then dissolved and the cobalt precipitated as NH_4CoPO_4 by the addition of $NH_4H_2PO_4$ (Hope's method). On ignition this precipitate changes to $Co_2P_2O_7$, and is weighed as such and the cobalt present calculated. The nickel is obtained by subtracting the weight of cobalt from the weight of cobalt + nickel previously found.

The Analysis.

As.—Weigh out ·25 gm. of the finely powdered sample of the ore. It must be remembered that as this ore is rich in arsenic, due precautions must be taken against loss by volatilisation during fusion. These precautions were given in the analysis of arsenical pyrites. The student may follow out the details of Dr Pearce's estimation as previously laid down. Duplicates should be run as usual, and the percentage of arsenic (As) reported.

Fe, SiO_2.—As this portion of ore will be used also for the estimation of nickel and cobalt, the amount of ore taken should be roughly proportioned to the probable amount of nickel and cobalt in the ore. With smaltine the amount of ore taken should run from 2 to 5 gms.; if in doubt, weigh out about 3 gms.

Transfer to a 200 c.c. flask. Add 10 c.cs. 36E. H_2SO_4, 10 c.cs. 16E. HNO_3, and 6 c.cs. 16E. HCl. Heat to decompose the ore, and continue heating till copious fumes of SO_3 are evolved. Cool, dilute to about 100 c.cs. and filter. Wash well with hot water. Reserve the filtrate.

Dry the filter and contents. Ignite, weigh, and report as percentage of *siliceous matter.*

Evaporate the filtrate to about 100 c.cs. Warm to about 70° C. and pass a rapid current of H_2S till a precipitate ceases forming. Allow the solution to cool towards the end of the precipitation.

Filter off the precipitated sulphide, washing well with H_2S water. Reserve the filtrate, and discard the precipitate of arsenic sulphide (unless any copper or other metals be present, when they should be estimated if a complete analysis is required). If the arsenic precipitates very slowly and comes down in the filtrate, pass SO_2 through the liquid to reduce the arsenic which is present in the *pentad* state. Boil off the SO_2 and treat again with H_2S. Filter and combine the filtrates.

Boil off the H_2S, adding a few c.cs. 16E. HCl and about ·5 gm. $KClO_3$ to oxidise the iron and sulphur. Boil down to about 100 c.cs.

Gradually add 5E. NH_4HO till the solution is decidedly alkaline. Filter off the precipitated $Fe_2(HO)$, washing once with hot water. Reserve the filtrate. Dissolve the precipitate in 5E. HCl, dilute with water, carefully neutralise with Na_2CO_3 as before instructed (see Separation of Fe and Mn by Basic Acetate precipitation), and precipitate the iron as basic acetate. This separates the iron from the small quantity of Ni and Co carried down in the ammonia precipitation. If the iron precipitate is large (it is not as a rule large with smaltine), the basic acetate precipitate should be redissolved and reprecipitated.

The two or three filtrates, as the case may be, are combined and reserved.

The basic acetate of iron is dissolved in dilute H_2SO_4 or HCl, and the iron estimated by standard $K_2Mn_2O_8$ or $K_2Cr_2O_7$ respectively. From the results, the percentage of iron (Fe) present is calculated and reported. Alumina is generally absent, but if present may be estimated as usual.

Ni and Co.—Boil down to about 100 c.cs. the combined filtrate from the basic acetate precipitation. Make the solution distinctly alkaline with 5E. NH_4HO. Transfer to a deep narrow 200 c.c. beaker and precipitate the nickel and cobalt by electrolysis on the kathode formerly used for the copper precipitation. The best conditions are ND_{100} = ·75 to 1 ampere; tension 2·8 – 3·3 volts, and a volume of about 150 c.cs. The ammonia added must be increased according to quantity of the metals present. The end of the reaction may be ascertained by testing with ammonium sulphide or potassium sulphocarbonate.

Treat the precipitated metals as before instructed—washing, drying, and weighing—the result being the weight of Ni + Co.

Separation of the Nickel and Cobalt (*Hope's method*).—Dissolve the nickel and cobalt from the kathode by treating in a 200 c.c. beaker with dilute HNO_3. When dissolved, wash down the kathode into the beaker with hot water. Evaporate the solution down to dryness, adding a few drops of 36E. H_2SO_4. When cool, dissolve the residue in about 50 c.cs. of hot water and heat to boiling.

Weigh out (approximately) about four times as much $NH_4H_2PO_4$ as there is nickel and cobalt present. Dissolve in the smallest possible quantity of water, add 3 c.cs. 5E. H_2SO_4 and boil (in a test tube). Add this mixture to the boiling solution of nickel and cobalt. Carefully add 5E. NH_4HO

till the precipitate partially dissolves. Continue adding the ammonia drop by drop till, with constant stirring, the cobalt comes down as a pink precipitate of NH_4CoPO_4. Heat for five to ten minutes.

Filter by decantation. Wash and dissolve the precipitate with a little 5E. H_2SO_4. Reprecipitate the cobalt by a small excess of $NH_4H_2PO_4$ and addition of NH_4HO as before.

Filter and wash with small quantities of hot water. Dry the precipitate and ignite in a platinum crucible over a bunsen for fifteen to twenty minutes; weigh as usual, and from the weight of $Co_2P_2O_7$ found calculate the percentage of cobalt (Co) in the ore.

As a check, the filtrates may be combined and brought to a bulk of about 200 c.cs., ammonia added, and the solution electrolysed (Hope recommends a battery of two one-and-a-half pint Bunsen cells, which will deposit ·15 to ·20 gm. nickel per hour; two to three hours being sufficient for the electrolysis).

The percentage of nickel may be calculated from the difference between the Co + Ni deposit on the kathode and the Co, calculated from the pyrophosphate precipitate or directly from the weight of Ni obtained in the second electrolysis.

Note. — The above description of Hope's method is taken from the abstract from the *Journal of the Society of Chemical Industry*, No. 4, vol. ix., April 30th, 1890, as published by C. & J. J. Beringer in the appendix to the 1900 edition of their well known text-book of assaying. For further information regarding the separation of nickel and cobalt consult the works of Furman, Beringer, and Classen—the last mentioned with special reference to the electrolytic determination of the metals. For information regarding the methods of analysis adopted in determining the nickel in ores consult *The Mineral Industry* (Scientific Publishing Co.), vols. viii. and ix. The analysis as given is interesting, in that it combines gravimetric, volumetric, and electrolytic methods.

(*h*) THE ANALYSIS OF CHROMITE.

The composition of this mineral when pure is 32% FeO and 68% Cr_2O_3, but, as a rule, MgO is generally present in amounts varying from 6% to 24%. The Cr_2O_3 may be partially replaced by Al_2O_3 and Fe_2O_3. CaO, NiO, or MnO may also be found.

As chromite (and some magnetites) is insoluble or only partially soluble in acids, this analysis has been selected to give the student further practice in the treatment of insolubles.

Method, Reactions, etc.—The student will find on consulting the various text-books and other literature on this subject that some ten to twenty variations of method of fusion are presented. The Beringers, in their text-book on assaying, tabulate twelve distinct fusion mixtures, some of which obtain the chromium in a form soluble in dilute acids—that is, as a chromic salt; others in a form soluble in water—that is, as an alkaline chromate.

Many of these mixtures will yield good results, provided due care be taken in the reduction of the mineral. For a successful fusion the mineral must be laboriously reduced to an almost impalpable powder. An extra twenty to thirty minutes devoted to the thorough reduction of the sample is amply rewarded by the subsequent saving of time otherwise wasted by repetition of the fusion.

In the method to be described (Genth's) the ore is first fused with $KHSO_4$ and then with Na_2CO_3 and KNO_3. The melt is dissolved in water

and evaporated to dryness with hydrochloric acid, the SiO_2 separated by filtration.

In the filtrate any chromates are reduced by alcohol. (Ferric salts are not reduced.) After boiling off the alcohol, ammonia is added. Filter, wash, and dry the precipitate of $Al_2(HO)_6$, $Fe_2(HO)_6$, $Cr_2(HO_6)$. This precipitate is fused with Na_2CO_3 and KNO_3. The melt is dissolved and the chromium oxidised to chromate by KNO_3. The iron and alumina are precipitated by ammonia, and then the filtrate is reduced by SO_2 and the chromium precipitated with ammonia, dried, ignited, and weighed as Cr_2O_3. Any MgO remains in the filtrate from the joint iron-alumina-chromium precipitation.

For other methods consult the works of Beringer and Furman, etc.

Details of Genth's Method.—(See *Chem. News*, 6, 31.)

SiO_2.—Powder finely in the agate mortar about 2 gms. of the ore. Take of this finely ground ore about ·1 gm. and grind exceedingly fine in the agate. Repeat with fresh portions until the sample has been thoroughly reduced. Time and labour are necessary to attain this end.

Transfer ·5 gm. finely reduced ore to a 25 c.c. platinum crucible. Mix with 10 gms. $KHSO_4$ and fuse over a good bunsen, commencing with a low flame and gradually raising the temperature. At the end of thirty minutes add 5 gms. anhydrous Na_2CO_3 and 1 gm. KNO_3 and fuse for another thirty minutes. For the last fifteen minutes a full red heat should be maintained. On cooling, swirl the 'melt' up the sides of the crucible.

When cool, transfer to a 300 c.c. beaker. Add 100 c.cs. water and digest till the melt is dissolved. Acidulate the solution (after removing and rinsing the crucible) with 16E. HCl. Evaporate to dryness in a porcelain dish. Take up with 10 c.cs. E. HCl and 50 c.cs. water. Filter and wash well with hot water. Reserve the precipitate. Evaporate the filtrate to dryness; take up as before and filter. This double evaporation and filtration is necessary to remove all the silica, which is estimated gravimetrically as usual.

FeO,Al_2O_3.—Evaporate the combined filtrates from the SiO_2 precipitations to about 150 c.cs. Add to the solution 15 c.cs. absolute alcohol and boil till the chromium is reduced to the chromic state (the alcohol is at the same time oxidised to aldehyde). Boil off the excess of alcohol (test by smell) and add a slight excess of 5E. NH_4HO. This precipitates $Al_2(HO)_6$, $Fe_2(HO)_6$, and $Cr_2(HO)_6$. There will probably be sufficient NH_4Cl present to prevent the precipitation of any magnesium salts present. If in doubt, dissolve the precipitate in excess of HCl and reprecipitate with NH_4HO. Combine the filtrates and reserve the combined filtrate.

Transfer the dried precipitate to a platinum crucible and fuse with about 2 gms. Na_2CO_3 and 1 gm. KNO_3. Fuse till perfectly liquid, finishing with a full red heat.

Cool as usual and dissolve the melt, removing and rinsing the crucible. Evaporate the solution (preferably in a platinum dish) to a semifluid state. Gradually add crystals of KNO_3 till effervescence ceases. Dilute with water, transferring to a beaker and making up to 100 c.cs. The chromium now exists as chromate. Add ammonia till just alkaline; heat to boiling, and filter off the precipitate of $Fe_2(HO)_6$, $Al_2(HO)_6$. Wash well, and reserve the filtrate, which contains the chromium. Estimate the Fe_2O_3 and Al_2O_3 as usual by difference, and calculate the Fe_2O_3 to FeO. Report as percentage of FeO and Al_2O_3.

Cr_2O_3.—The last filtrate is reduced by passing a brisk current of SO_2. The excess of SO_2 is then boiled off and the chromium estimated as described under "Simple Quantitative Analysis." Report the result as percentage of Cr_2O_3.

MgO.—The combined filtrate from the iron-alumina-chromium precipitations (the first reserved filtrate) is evaporated to a suitable bulk, and precipitate the magnesia as previously instructed. Incinerate, weigh, and report the results as MgO.

Note.—Generally in chromite the only estimation required in practice is that of Cr_2O_3; the various operations are accordingly cut down to those necessary for the solution, separation, and precipitation of the chromium.

In this and other cases where a fusion is necessary it may be allowable to neglect the full qualitative analysis, provided the sample be recognised as a silicate or other infusible, and also that all the likely constituents are assumed to be present. When analysing rocks this practice may be safely followed, as the student knows what elements can be present and conducts the analysis accordingly; but when examining minerals the usual rule should be followed—the qualitative analysis should be first conducted. The student must remember that in the routine of professional work the demonstrator does not present him with a mineral, tell him what it is, and what estimations are required. Information given by forwarders of specimens concerning the nature of the specimen is frequently wrong, and for this and other reasons the student should cultivate the habit of treating every sample given to him as if it had been handed to him by some one ignorant of analytical methods, who looks to the student to tell him what the substance is both qualitatively and quantitatively.

CONCLUDING NOTE TO PART II.

The metallurgical student has so far been taken through a course of analysis (inorganic) comprising the qualitative analysis of simple and complex salts, including insolubles, and expanded to include alloys, minerals, and metallurgical products. Following this, he has taken a course of instruction in quantitative analysis, commencing with the necessary manipulation and adjustments of weighing and measuring apparatus, followed by simple gravimetric analysis, volumetric analysis, gasometric analysis, electrolytic analysis, and a selection of a few typical examples of mixed or complex analyses.

Throughout this work (wherever possible) the equivalent system of reagents has been employed, and the student who grasps the principles of this system and carries them into practice will acquire a much more accurate knowledge of the subject than the student who blindly uses reagents concerning the exact strength of which he has frequently but a very hazy idea. The authors have found some difficulty in carrying the system through the quantitative work owing to the varying volumes of reagent, often of varying strength, advised by different chemists. It is hoped that in the near future the details of analytical methods will be stated more accurately than in the past as regards volume of solution, concentration of salts in solution, temperature of solutions, fusions, etc., time of ignition, necessity of reprecipitations, and other points of vital importance to accurate work.

In Part III. the student is introduced to a course of work in fire-assaying, and a brief course of selected examples of technical analyses.

PART III.

ASSAYING.

CHAPTER I.

INTRODUCTORY.

THE student who has conscientiously followed out the course laid down in Parts I. and II. of this work will now be in a position to *intelligently* undertake a course of work in assaying, it being presupposed that the student has obtained a fair knowledge of chemical theory, the chemistry of the non-metals and metals.

The course laid down in the following pages has been selected on the assumption (as regards time) of a minimum of 16 hours per week for 33 weeks. The authors, while admitting that the ground might perhaps be covered with more speed, urge that where skill and confidence are to be obtained only by practice, too much time cannot be devoted to such practice, therefore the student who can by any means afford the time is advised to extend the above minimum as far as possible.

When, in the laboratory, an unexpected result is obtained, such a result should not be passed over as a mere accident, but should be investigated until some satisfactory explanation has been obtained, for here, as in the previous courses in chemical analysis, it will be found that there is a reason for everything—that nothing occurs by mere chance. If an expected reaction does not take place some interfering cause or causes must be at work, and it is the duty of the conscientious student to discover such cause or causes. The additional time given to the thorough solution of problems frequently met with in the routine of laboratory work will be amply compensated for by the additional confidence felt by the student when he realises that he is becoming capable of mastering difficulties which otherwise would master him.

DEFINITION AND SCOPE OF THE TERM 'ASSAYING.'

In recent literature the term 'assay' is of very wide application. Certain works, for instance, treat of the 'assay' of drugs and other vegetable substances. It seems more fitting that the definition of the term be restricted to the determination of the commercially important elements in their ores, alloys, or similar products, and that the term 'analysis' be applied to other determinations. Reference to the literature on the subject will show how varied is the definition of this term — a variation of definition ranging from pure 'fire work' to 'general analytical work,' involving, with some extremists, the estimation of certain organic compounds in drugs.

In modern metallurgical practice the demands made on the assayer are gradually increasing. Besides being expert in the fire-assays of gold, silver, lead, tin, etc., he must have a thorough knowledge of 'wet methods' as applied to several of the foregoing elements, and more especially as applied to the estimation of copper, iron, zinc, and other elements. He must be competent in volumetric, gravimetric, and electrolytic methods, and in certain technical methods of gas, water, and other analyses. The demand thus made on the resources of the assayer is gradually becoming more severe, and necessitates a more thorough and a wider grasp of general inorganic chemistry than was hitherto considered essential.

As metallurgical science is ever growing, it is but natural to expect that its demands on its ally, assaying, will likewise increase; and that the supply should meet the demand, it is absolutely essential that the modern assayer should have a thorough grounding in theoretical and practical chemistry, else he will be a mere rule-of-thumb worker, incapable of the least original work, and therefore of little use to his employers when they most need advice and assistance.

CLASSIFICATION OF METHODS OF ASSAYING.

Assuming that assaying be defined as "the estimation of the commercially important elements in their ores, alloys, or products," the following classification of methods, though not exhaustive, may be adopted for convenience.

METHODS OF ASSAYING.

I. Dry (or Fire).

II. Wet.
- (*a*) **Gravimetric.**
- (*b*) **Electrolytic.**
- (*c*) **Volumetric.**
- (*d*) **Gasometric.**
- (*e*) **Colorimetric.**

As examples of these methods repeatedly come under the student's notice, only a few words of explanation will be given here.

I. Dry (or Fire) Methods.—These methods involve the direct application of heat by one or more of the following operations:—

Fusion and *Reduction*, *Scorification*, *Cupellation*, *Roasting*, *Distillation*. Many of these operations are followed by *Inquartation* and *Parting*. These operations have not been included in the foregoing tabulation of methods, as in most cases each operation by itself does not constitute a complete method of assaying, but requires the help of one or more of the other operations mentioned. The operations themselves will be described in detail further on.

II. (*a*). **Gravimetric Methods.**—These methods are distinguished in that the element sought for is isolated in such a form (generally as a chemical compound) as to be estimated by weighing on the balance (see Quantitative Analysis, Part II.).

II. (*b*). **Electrolytic Methods.**—These methods are distinguished in that the element sought for is deposited in a weighable form (generally as the uncombined element) by the agency of the electric current. (See Electrolytic Analysis, Part II.)

II. (*c*). **Volumetric Methods.**—These methods are distinguished in that the element sought for is obtained in such a state that it may be estimated by the direct measurement of the volume of a liquid. (See Volumetric Analysis, Part II.)

II. (*d*). **Gasometric Methods.**—These methods are distinguished in that the element sought for is obtained (free or combined) in the gaseous state, and is then estimated by measurement of its volume. (See Gasometric Analysis, Part II.)

II. (*e*). **Colorimetric Methods.**—These methods are distinguished in that the element sought for is estimated by a combination of volumetric methods (II. *c*.) and the determination of colour tints. (See Colorimetric Analysis, Part II.)

CHAPTER II.

REAGENTS.

A **Reagent** may be defined as a substance that reacts, that is, brings about some chemical change.

The student will by this time be quite familiar with many reagents employed in qualitative and quantitative chemical analysis. A new class of reagents will now be considered — a class the majority of the members of which require the aid of considerable heat before they fulfil their function.

The following tabulation includes the most important reagents used in 'fire' assaying. The majority of these reagents are solids, though a few liquids are employed. The terms employed are defined as follows:—

A **Reducer** is a substance capable of removing *oxygen* from its combinations.

An **Oxidiser** is a substance capable of readily giving up *oxygen* to other substances.

A **Flux** is a substance which by forming fusible compounds readily brings about the fusion of otherwise refractory substances.

The terms **Sulphuriser** and **Desulphuriser** explain themselves. Also the term **Solvent**, molten lead, *e.g.* for dissolving gold.

The terms '**Absorbent**' and '**Cover**' will be fully explained further on, as also will be the terms '**Inquartation**' and '**Speise.**'

REAGENTS FOR FIRE-ASSAYING.

Reducers.	Oxidisers.	Fluxes.	
		Acid.	Basic
Charcoal. Flour. Argol. Potassium Cyanide. Sulphides. etc	Nitre. Red Lead. Litharge. Carbonate of Potassium. Bicarbonate of Sodium. etc.	Silica. Borax. etc.	Fluor-spar. Quick-lime. Magnesia. Alumina. Carbonate of Potassium. Bicarbonate of Sodium. Litharge. Lead. Nitre. Argol. etc.

REAGENTS FOR FIRE-ASSAYING—*continued.*

Desulphurisers.	Sulphurisers.	Absorbent.	Solvent.
Iron. Potassium Cyanide. Litharge. etc.	Sulphur. Galena. Stibnite. etc.	Bone ash.	Lead.
		Inquartation.	**Cover.**
		Silver.	Salt. Borax.

Wet Reagents.			Speise-former.
Distilled Water.	Nitric Acid.	Sodium Thiosulphate.	Arsenic.

Considering in detail these reagents, the first group is that of the **reducers.** The following equation represents the action of **charcoal** on litharge when subjected to a red heat in a crucible,

$$2PbO + C = Pb_2 + CO_2$$

Litharge and carbon yield lead and carbon dioxide. When the student comes to the practical testing of the strength of reducers he will find that charcoal is a very powerful reducer, and that it is more advisable in many cases to employ a weaker reducer, such as flour or argol. By employing a weaker reducer it is found that, owing to its greater quantity, it can be more readily and thoroughly mixed with the ore, and also that less care need be exercised in weighing the reducer, as a difference of a few grains more or less of argol makes much less difference in the weight of the resulting lead button than a similar difference in the use of charcoal.

The reducing power of **flour** depends chiefly on its carbon contents; and as these vary slighly with the different 'brands' of flour, the reducing power will be found to vary correspondingly.

Argol is a crude bitartrate of potassium (formula $KHC_4H_4O_6$). This reducer is of much service to the assayer, being fairly constant as regards reducing power; and further, is of a convenient strength for much of the routine work of the fire-assayer.

Potassium Cyanide—(KCN).—This salt is largely used in the fire-assays of tin and lead ores, and acts as a reducer towards the oxides of these metals, cyanates being formed as shown in the equation

$$SnO_2 + 2KCN = Sn + 2KCNO$$

metallic tin and potassium cyanate being formed.

The following tabulation gives the reducing powers of some of the chief reducers as well as of certain substances, such as **sulphides,** which are found in certain ores which come under the assayer's notice. These sulphides act as reducers to substances such as litharge, the sulphur uniting with the oxygen of the litharge, metallic lead being deposited, and the metal of the sulphide either remains free or combines with other substances present to form a slag. When, for example, it is stated that the reducing power of a

substance is 13, it is understood that one part by weight of the reducer is capable of reducing 13 parts by weight of lead from litharge. Twenty grains of this reducer mixed with excess of litharge (in a crucible and heated to a bright red) will reduce a lead button of $20 \times 13 = 260$ grains.

REDUCING POWERS.

Good Wood Charcoal,	25 to 30
Coke,	24
Hard Coal,	24 to 25
Flour (Wheat),	11 to 13
Common Starch,	11½ to 13
Crude Argol,	6 to 8
Iron Pyrites,	8
Copper Pyrites,	7
Cream of Tartar,	4 to 6

The student must remember that these figures are only approximate, and that on trial he may obtain results varying one or two units from the figures given, the reason being that such substances are rarely, if ever, obtained in a state of purity, and the impurities contained are by no means constant in different samples of the same material.

OXIDISERS.—Under this heading come a number of substances capable of giving up all or part of their oxygen contents to other bodies, on the application of heat. The oxidising power of these substances may be determined by chemical calculations based on their behaviour on the application of heat. Thus we may compare the oxidising powers of **Nitre** (KNO_3) and **Red Lead** (Pb_3O_4) if we know the chemical reactions taking place between the oxidiser and the substance oxidised. If a mixture of KNO_3 and metallic **Pb** be heated the following reaction takes place—

$$KNO_3 + Pb = KNO_2 + PbO$$

Heated with carbon the following reaction occurs—

$$4KNO_3 + 5C = 2K_2CO_3 + 3CO_2 + 2N_2$$

Red Lead (Pb_3O_4) when heated above 450° C. yields up part of its oxygen thus—

$$Pb_3O_4 = 3PbO + O$$

The oxygen thus set free is ready to unite with and oxidise other elements present. This reagent may be used in place of litharge when dealing with pyritic ores, sulphur being oxidised, and metallic lead left as a collecting agent for gold and silver.

It must be remembered that oxidation and reduction are two processes which must often be regarded as the complements the one of the other, that is, when one substance is oxidised another substance is frequently reduced. As an illustration, the action of charcoal on red lead may be cited. The charcoal reduces metallic lead from the red oxide, and at the same time the oxygen of the red oxide oxidises the charcoal, forming oxides of carbon. Concerning these and like reactions the student will find full information in any of the well known text-books on the chemistry of the metals and non-metals. The student who has a fair grasp of the principles of theoretical

chemistry will find little difficulty in understanding the various reactions of oxidation and reduction employed in the various processes of fire-assay.

Fluxes.—These have already been defined as substances employed to promote the fusion of refractory substances. Complex substances are formed whose melting points are much lower than those of their refractory constituents.

That the student may intelligently employ such substances, he must (1) know the approximate composition of the ores he is dealing with; and (2) this being known, he must understand the nature and use of his fluxes.

The Composition of Ores.

Some knowledge of mineralogy will be of service to the assayer in determining the nature of ores. In most cases the ores dealt with by the fire-assayer consist chiefly of either oxides or sulphides, though minerals containing tellurium or antimony, arsenic, etc., are not infrequently met with in ores.

The following brief tabulation, though not at all exhaustive, embraces the majority of ores dealt with by the fire-assayer.

I. **Oxidised Ores.** { *Acid.* / *Basic.*

II. **Sulphide Ores.**

III. **Ores** containing **Tellurium, Arsenic, Antimony, Bismuth,** etc.

I. **Oxidised Ores**—*Acid.*—Gold-bearing quartz may be taken as a typical example of this class of ores.

Oxidised Ores—*Basic.*—Ores containing a fair percentage of one or more of the following oxides, etc.—Limonite, Magnetite, Calcite, Dolomite, and Schistose or slaty substances.

II. **Sulphide Ores** (sometimes termed **Pyritic** ores or **Sulphurets**). These may contain one or more of the following sulphides (as well as traces of minerals found in Class III.), sulphides of iron, lead, copper, zinc, etc.

III. **Ores of this class** embrace those containing in appreciable quantity arsenic, antimony, bismuth compounds, tellurides of gold, silver, etc.; in brief, all ores coming under the assayer's notice and not classified under groups I. and II.

Schemes for the examination of unknown ores prior to fire-assay have been given on preceding pages. These schemes serve as a guide to the student; the professional assayer can, from experience and his knowledge of mineralogy, generally determine by inspection the nature of an ore submitted for assay.

Having briefly considered the nature of the ores to be dealt with, the action of fluxes will now be discussed. The metallurgical student, in his study of the metals and the principles of metallurgy, will have received the 'grounding' necessary to the intelligent use of these reagents; he has now to apply his knowledge.

FLUXES.—It will be seen that these are divided into two classes, **Acid** and **Basic.** A general rule may be laid down that an acid ore requires a basic flux and a basic ore an acid flux. That this is based on chemical principles will be seen on considering the nature of the complex silicates and borates occurring in the 'slags' formed by the fusion of ore and flux. Some 'slags,' especially those crystallized, have a definite chemical composition corresponding to a definite formula, whilst others are simply mixtures of different silicates. The following table gives the composition of the more important silicates.

	A	B	O in Base : O in Acid
Subsilicate, . .	$4RO,SiO_2$	$4R_2O_3,3SiO_2$	2 : 1
Monosilicate, . .	$2RO,SiO_2$	$2R_2O_3,3SiO_2$	1 : 1
Bisilicate, . .	RO,SiO_2	$R_2O_3,3SiO_2$	1 : 2
Trisilicate, . .	$2RO,3SiO_2$	$2R_2O_3,SiO_2$	1 : 3
Sesquisilicate, . .	$4RO,3SiO_2$	$4R_2O_3,SiO_2$	2 : 3

In column A the SiO_2 is united with an oxide such as **FeO**, and in column B with an oxide such as Fe_2O_3.

A silicate containing one base is termed a **Monobasic** or **Simple Silicate**; two bases a **Double Silicate**, and so on. The fusibility of slags is dependent on the amounts of silica and bases they contain.

The subsilicates are very fusible, the monosilicates less so, and the bi- and tri- less so still; that is, as the proportion of base diminishes, the fusion point rises. Again, double silicates are more fusible than simple silicates. The mixture of two bases seems to behave similarly to a mixture of metals in an alloy—the melting point is lowered. The most fusible silicates are those of the alkalies, then those of lead, manganese, iron, copper, etc.; then those of the alkaline earths. For further information the student is referred to metallurgical treatises dealing with blast furnace charges.

The borates are another set of complicated compounds of some importance to the assayer. Some knowledge of the action of borax on bases has been obtained by the student in the course of blowpipe analysis. Borax acts as a flux for oxides of iron, lime, etc.

The chief acid flux, then, is *silica*, and in the column of basic fluxes will be found the names of a number of substances, the chief of which for the assayer's purpose are the *carbonates of sodium* and *potassium*, *litharge* and *fluor spar*. These fluxes with silica form silicates of sodium, potassium, lead, and calcium, whilst the **fluorine** is of service in breaking up silicates. A mixture of K_2CO_3 and Na_2CO_3 alone or with other reagents is of much service in breaking up certain clays which are decomposed with difficulty when either carbonate is used alone. **Litharge** is a most powerful basic flux, besides being an 'oxidiser' and 'collectant' for gold and silver. As a 'flux' it combines with silica, forming silicates of lead. Also with certain 'infusible' oxides such as red oxide of copper, it is capable of uniting to form fusible compounds.

DESULPHURISERS AND SULPHURISERS.

These terms explain themselves, the following equations showing the reactions:—

Desulphurisers—

$$PbS + Fe = FeS + Pb$$
$$PbS + KCN = KCNS + Pb$$
$$PbS + 2PbO = SO_2 + 3Pb$$

Sulphurisers—

$$Fe + S = FeS$$
$$Fe + PbS = FeS + Pb$$

Sulphur acts as a reducer towards litharge, metallic lead being deposited and sulphur dioxide formed.

ABSORBENTS.—Bone Ash.—This substance is much used in making cupels, it being capable of absorbing the litharge formed on subjecting molten lead to an oxidising atmosphere. Bone ash prepared from the bones of horses and sheep is considered the best. This reagent is obtained ready for use, and for convenience a little may be sifted through muslin and bottled. This fine ash will be found useful for sprinkling on top of the coarser ash in the cupel mould when a cupel with a fine surface is required.

SOLVENTS.—In fire-assaying metallic lead is used as a solvent for gold and silver. The lead is used sometimes in the granulated form, but more often it is obtained in minute globules by the action of a reducer on litharge. A shower of such globules on permeating the charge in a crucible picks up particles of gold and silver and collects them into a button at the bottom of the crucible.

COVER.—Salt alone or salt and borax may be used as covering agents. The salt on melting floats in a layer on the top of the charge, and prevents oxidation by excluding the air. A pinch of salt tends to prevent the too violent ebullition of a charge, the action here being somewhat similar to that of oil on water.

INQUARTATION.—Test Silver.—This will be required in the operation of *Inquartation*, to be described later on. To be suitable for this purpose the silver must contain *no gold*, and otherwise must be reasonably pure. A little copper will in many cases do no harm, thus allowing the use of silver coin; but if pure test silver be required, it may be prepared as follows :—

A silver coin or piece of bullion is placed in a small beaker; add about 20 c.c. strong HNO_3, gently heat in a fume chamber till all is in solution. Precipitate the silver as AgCl by slowly adding HCl until a slight excess is present. Boil for a few minutes, dilute with water, and filter. Wash the ppt. well with boiling water.

Test silver is frequently prepared from waste silver solutions. The silver in these is precipitated by adding salt (avoiding excess). The resulting AgCl is washed by decantation and then boiled in aqua regia to dissolve any gold present. Wash again and pure AgCl is obtained.

This AgCl may be treated in one of two ways—(*a*) by fusion with reducer and flux, or (*b*) reduction to Ag by Fe or Zn.

(*a*) **By Fusion.**—This method, though speedy, results in the loss of a certain amount of silver by volatilisation, etc.

The chloride is dried, weighed, and smelted in a small clay crucible (D), after mixing with the following charge—

AgCl	1 part
Glass Powder	1 part
Soda	1 part

Cover, a little borax and 8 or 10 grains of nitre.

Fuse in a hot fire; pour when tranquil into a hot clean mould. When cool, detach and clean the button from slag. If foil be desired, pass repeatedly through the rolls. If granulated, remelt and pour from a height of about 6 feet into a bucket of cold water.

(*b*) **By Reduction.**—Place the moist AgCl in a porcelain basin, add sheet zinc strips in the proportion of one part Zn to two parts Ag. Add a *little* H_2SO_4. Let stand over-night. Add more H_2SO_4 if any Zn is still undissolved. Wash the 'cement' silver well, dry and weigh. Fuse in a small plumbago crucible with a cover of charcoal powder, adding a little 'borax glass' and a *small* pinch of nitre. When melted, pour into a mould. Further treatment as in (*a*).

Before proceeding to the preparation of wet reagents, a short description will be given of the preparation of pure gold.

Proof Gold.—Weigh out about 100 grains 'gold cornets' (see Bullion Assaying). Place in a small flask (500 c.c.). Add gradually 50 c.c. aqua regia. Heat gently to boiling on a hot plate. When all the gold is dissolved, dilute with water to about 400 c.c. Stand a few hours; decant the solution from any precipitated **AgCl** into a large evaporating dish; evaporate till nearly all the acid is expelled and $AuCl_3$ begins to separate out. Dilute to about 400 c.c. and filter into a glass flask (500 c.c.) through a double filter paper. Plug the neck of the flask with cotton-wool, stand for 4 to 6 days. Decant about seven-eighths of the solution through a filter paper; neglect the remainder for the present. Heat to boiling, and add an excess of a saturated solution of oxalic acid till the solution is colourless. Stand over-night. Pour off the solution and wash well with warm distilled water, then with ammonia water, then again with distilled water. Wash with dilute **HCl** and again with distilled water. Transfer the gold to a porcelain dish. Dry, fuse in a clean crucible in which some borax has been melted. Cover with borax glass and add a few grains of nitre. Pour into a clean waxed mould. When cool, detach the button from the slag, clean thoroughly, and pass through the rolls. The resulting gold should be about 999·95 fine.

WET REAGENTS USED IN FIRE-ASSAYING.

Water.—This is used chiefly for washing 'beads' or 'cornets' of gold after inquartation and, as silver nitrate is present, the water used must be free from chlorine; therefore if tap-water be used it must give no reaction for chlorine. If chlorine be present the water must be distilled; and where a considerable quantity of distilled water is required, a self-filling copper still of one or two gallons capacity will be found convenient.

Nitric Acid for 'Parting.'—This reagent is used for dissolving the silver from an alloy of silver and gold; and here again, as silver nitrate is formed, chlorine must be absent. Generally, nitric acid can be obtained free from chlorine, but if not, the chlorine may be precipitated by the addition of silver nitrate. A precipitate of silver chloride is obtained, from which, after standing for some days, the acid may be syphoned off.

For ordinary work the following solutions are made up:—

No. 1.—1 volume strong HNO_3 + 2 volumes water (dist.).
No. 2.—1 „ „ „ + 1 „ „ „

Where the bead consists largely of silver, No. 1 solution alone may be sufficient, but in many cases the No. 2 solution must also be used. A little silver nitrate may be added to these solutions as a precaution against chlorine. Nitrous acid may be present; and as this acid is a solvent for gold, any traces present must be driven off by boiling for a few minutes before use.

For bullion assays the Mint and Bank assayers generally make up their solutions as follows:—

No. 1.—S.G. 1·16 (21° Beaumé)
No. 2.—S.G. 1·26 (32° Beaumé)

For No. 1 solution, 8 parts HNO_3 (S.G. 1·41; 44° Beaumé) mixed with 15 parts distilled water make an acid of S.G. 1·16 (21° Beaumé).

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For No. 2 solution, 8 parts HNO_3 (S.G. 1·41; 44° Beaumé) mixed with 5 parts distilled water make an acid of S.G. 1·26 (32° Beaumé).

The practice of many American assayers is to use for beads from ores only one acid of S.G. 1·20 (26° Beaumé), and for bullion work the two solutions given above of S.Gs. 1·16 and 1·26.

Sodium Thiosulphate (Hypo) $Na_2S_2O_3,5H_2O$.—This salt is serviceable for the Russell process extraction tests for the solution of silver chloride.

Besides the reagents mentioned, the assayer will find it convenient to have beside him a set of the more common chemical reagents, including the strong acids and alkalies; also numerous materials such as oil, plumbago, etc. etc., which will be mentioned from time to time.

CHAPTER III.

THE ASSAY LABORATORY: ITS FITTINGS, APPARATUS.

THE ASSAY LABORATORY.—For fire-work a room should be set aside, and for convenience it should be situated near the balance room and the chemical laboratory. Gas and water must be laid on if possible, and provision must be made for lighting by day and night (if necessary).

The modern assay laboratory frequently errs on the side of over-equipment. The assayer many times in his after-career has to work without gas and many other luxuries found in large laboratories. It would be well, then, for the student to remember that a 'coke-' or 'coal'-fired muffle, besides being suitable for cupellation, can be readily adapted to the needs of the chemist. Incinerations, silicate fusions, etc. can with care be accurately performed in the muffle.

Again, a small blast kerosene stove, costing from ten to twenty shillings, can be surmounted by an iron plate or sand bath suitable for boiling, evaporation, etc.

The student may, without unduly interfering with his work, spend some time in exercising his wits on the construction of apparatus. Some of the finest chemical research has been carried through with home-made apparatus; and he should remember that here, as in many other cases, more depends on the skill of the operator than on an elaborate equipment.

No attempt will be made to furnish detailed plans, but a few general points may be noted:—

Floor; preferably of concrete. **Roof**; slate or iron (painted), and ventilated by a 'lantern.' **Walls**; preferably of brick. **Benches** and **Lockers**; of wood, and placed round the walls. **Furnaces**; in the centre of the laboratory.

Fume cupboards, gas, water, grinding appliances, rolls, etc. etc., may be fitted where most convenient.

Besides the laboratory proper, a special room must be set aside for the finer balances. The tables on which these are placed must be of solid construction, and designed to reduce vibration to a minimum. Provision must also be made against dust and fumes from the assay and chemical laboratories.

FITTINGS, FURNACES.

Two types of furnaces are required for the efficient performance of the work of the fire-assayer; these are, melting or wind furnaces and muffle furnaces. Many varieties of design are on the market, much depending on the nature of the fuel used, which may be either gaseous, liquid, or solid.

Furnaces for Gaseous Fuel.—These furnaces are designed to consume ordinary illuminating gas, and are simply large and modified bunsen burners. They give good results if carefully handled and regularly cleaned, but can only be recommended where gas is cheap; and as the assayer can but rarely obtain gas at a low figure, the student should, at least at the outset, confine

his attention to some other form of furnace. Figures 73 and 74 represent two common forms of Gas Melting and Muffle Furnaces respectively.

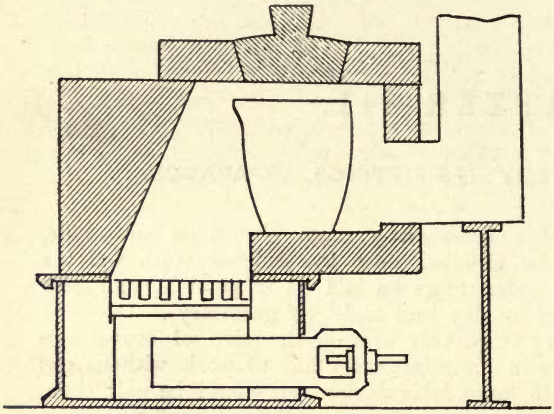

FIG. 73.

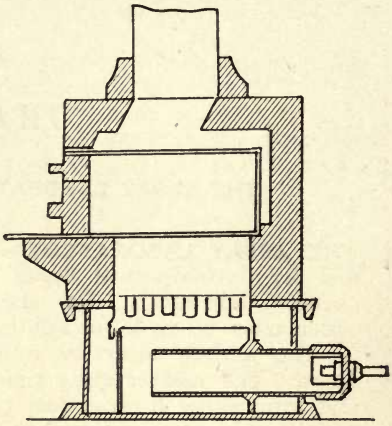

FIG. 74.

Furnaces for Liquid Fuels.—During the past ten years this type of furnace has been brought to great perfection, and portable outfits for melting and cupellation can now be had at a reasonable figure. The outfit consists of three parts,—the oil-reservoir and pump, the burner, and the furnace proper. In out of the way places, where coal or coke is unobtainable or very expen-

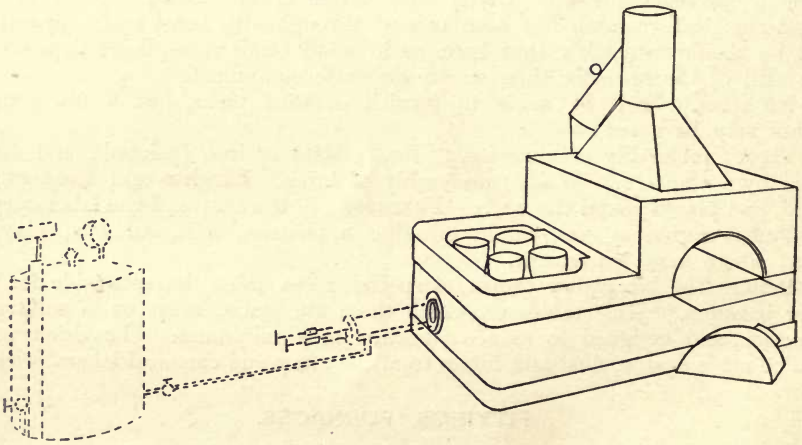

FIG. 75.

sive, this outfit is very serviceable, as the 'oil' or 'gasoline' can easily be transported, the volume of oil required being much smaller than that of coal or coke for equal heating effect. Very many varieties of these furnaces are obtainable, some of them displaying much ingenuity. Figure 75 shows a combined Melting and Muffle Furnace.

If gasoline be used as fuel, special care must be taken in following out the directions given regarding the storage and use of this dangerous liquid.

The makers generally supply full instructions regarding the setting up and operation of the furnace.

Furnaces for Solid Fuels.—The fuel used may be coal, coke, or char coal; generally coke or coal. For the 'wind' furnace coke is the most suitable fuel, though for the 'muffle' furnace, coal has certain advantages over coke; the muffle may be 'underfed,' the fuel being fed underneath and not on the top, thus prolonging the life of the muffle; any free-burning coal may be used, one cwt. of coal running an 8″ × 14″ muffle for eight hours. With ordinary prices a saving in fuel as compared with coke results. The fire is quickly started, and the temperature is readily controlled.

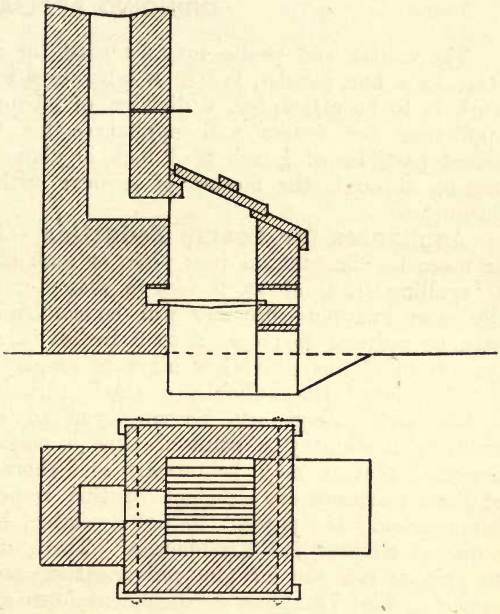

FIG. 76.

The melting furnace may be constructed of red brick, with a lining of firebrick. It should be provided with movable fire bars, a cast iron top, and a damper to regulate the temperature. Figure 76 shows a convenient design.

The muffle furnace will vary in design according to the nature of the fuel used. In some of the later designs of coal-fired muffle furnaces, two muffles are employed, the one above the other, the upper being used for cupellation and the lower for scorification. Figure 77 shows a furnace designed for the use of coke, and figure 78 a design for a free-burning coal (preferably bituminous).

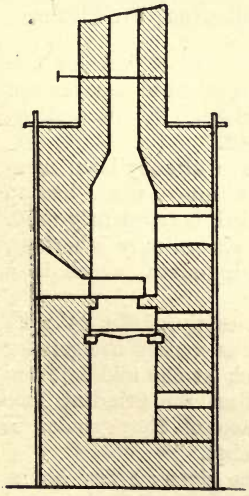

FIG. 77.

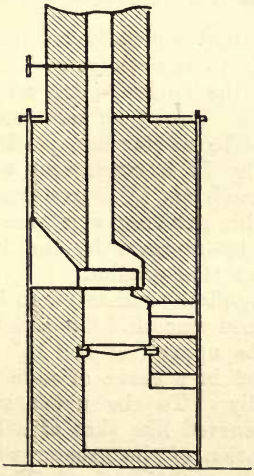

FIG. 78.

Fire-brick may be used in the construction of these furnaces, though red brick answers well if supported by angle iron and straps. A damper to regulate the temperature will be found very convenient, though not absolutely necessary.

Where proper furnaces were not available, assays have been conducted successfully in an ordinary kitchen range, or on a blacksmith's forge, with the aid of a small flower-pot for a muffle. For such impromptu

appliances the wit and resources of the assayer must be depended on, and in the course of his work the student will have the opportunity of noting where he may replace, partially at least, the appliances of the laboratory by those of everyday use.

GRINDING APPLIANCES.

The mortar and pestle may be used for reducing an ore from the coarse state to a fine powder, but in a laboratory where any considerable amount of work is to be attempted, a division of labour must be adopted by providing appliances for coarse and appliances for fine reduction; by 'coarse' is meant particles of $\frac{1}{8}$ inch to $\frac{1}{2}$ inch in diameter; by 'fine' is meant particles passing through the meshes of a sieve with, say, 20 to 120 holes to the linear inch.

Appliances for Coarse Reduction.—For pieces of ore 9 to 12 inches or more in diameter an iron plate or slab about 36″ × 36″ × 4″ (cast iron); a 'spalling' ring about 2 feet in diameter and 4 inches deep and a heavy sledge or knapping hammer will be convenient. By this means the lump may be reduced to pieces 2 to 3 inches in diameter. For further reduction some form of fine pulveriser must be employed.

If 'power' be available, a small rock-breaker driven from shafting by a belt and pulleys can be employed to advantage. Here, as in other reducing machinery, a point of vital importance is that the machine be so designed that it may be quickly and thoroughly cleaned. Many otherwise efficient machines are deficient in this respect, and cannot therefore be recommended. If 'power' be not available, the same type of machine can be obtained adapted for hand-power. These machines can readily be adjusted to prepare the ore for fine pulverisation on the bucking-plate, or by other means. Fig. 79 shows a convenient form of pestle and mortar.

Where expensive machinery is unobtainable the prospector's 'dolly' can, with a little ingenuity, be adapted to the needs of the assay office.

Apparatus for Fine Reduction—(*a*) Grinding Appliances; (*b*) Sieves.

For coarse reduction sieves may generally be dispensed with, but for fine reduction they are indispensable to the student. The experienced assayer can with care reduce a sample on the bucking-plate without the aid of a sieve, but to the beginner this practice cannot be recommended.

(*a*) **Grinding Appliances.**—The mortar and pestle have already been mentioned. The form shown in fig. 79 is convenient where much work has to be done. The short pestle, though not to be recommended, is frequently used. It may be safely stated that this grinding appliance is exceedingly laborious, and wherever possible should be replaced by the bucking-plate, which is a cleaner and much more efficient 'fine-grinder.'

The simplest form of bucking-plate consists of an iron casting 18″ × 24″ × 1″, the upper face of which is planed smooth. On this face is worked the grinder of cast iron, about 4″ × 6″ on the upper face and $1\frac{1}{2}$″ thick at the middle, from which, on both sides, it falls off in a curve of wide radius, the grinding face being planed true longitudinally. To the upper surface of the grinder is attached a handle, preferably curved like that of a hatchet.

No description of the operation of the grinder will be given; a few hours' practice will teach more than pages of writing. Fig. 80 shows the plate and grinder.

The form shown is simple, and if placed overlapping the edge of the table

or other support by about 2 inches the powdered ore is easily brushed off into a scoop or on a sheet of paper. The two longer edges of the plate are often provided with raised flanges to confine the ore. Some makers pivot the plate at the two sides so that it may be tilted for cleaning, but this seems to be an unnecessary refinement. A radical modification of the plate and grinder has recently been placed on the market by an American firm, and combines the grinder and sieve. The pressure between the grinder and plate is adjusted by simple spiral springs, whilst an ingenious design of the grinder provides a regular feed of ore. The principle of the machine seems good—the feed being regular, the ore being discharged *as soon* as fine enough, and the pressure permitting of easy adjustment.

(*b*) **Sieves.**—These are generally designated as 20, 30, 40 . . . 100, etc., according to the number of meshes per linear inch, a 20 sieve having 20 holes per linear inch, that is 400 holes per square inch, an 80 sieve having 80 holes per linear inch, or 6400 holes per square inch, and so on. A convenient diameter of sieve is nine inches. It is important when selecting a sieve to choose one that can be readily inspected and cleaned. The most suitable material for the wires is brass; for the body, wood or iron. For general purposes the following sizes will be useful:—20, 40, 60, 80, 100.

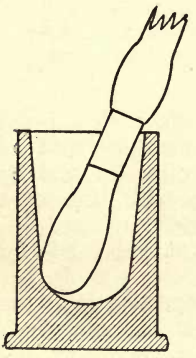

FIG. 79.

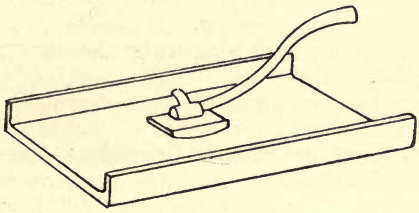

FIG. 80.

These sieves may be had in box sets provided with a lid and receiver, thus retaining the dust. The student will find that, when dealing with an ore which clogs the meshes, the operation of sifting is much hastened by placing in the sieve along with the ore two or three small copper coins; if copper be harmful, discs of some other metal may be employed. The student is reminded finally that he must be *absolutely certain* of the cleanliness of all reducing and sifting apparatus *before* proceeding to crush a sample of ore.

GENERAL FITTINGS, APPARATUS, ETC.

The following list of headings, though by no means complete, includes the most important of the smaller pieces of apparatus necessary in the assay laboratory.

Crucibles.—These are made of various materials, and are known as "Clay," "Graphite," "French Clay," "Hessian," etc.

"Clay" Crucibles.—These are best suited for the assays of gold, silver, lead, and tin ores. In the selection of a crucible for a particular assay, the nature of the charge must be taken into consideration; for a basic charge a basic crucible should be chosen, and *vice versa*. The student will note that when fusing certain charges in these crucibles it is necessary that some

substance, such as silica, be added to protect the crucible. Experience will prove to him that with some ores a crucible may serve for three or four fusions, whilst with other ores it may barely serve for one. The cause of this may be discovered by the exercise of a little reasoning, based on the student's general knowledge of chemistry. Figures 81 and 82 show the round and triangular forms of these crucibles. The round form is perhaps the better, and convenient sizes for the student's work are those marked D, E, F, G,—D being the smallest and G the largest of the four mentioned. For ordinary purposes a good crucible should be infusible at a bright red

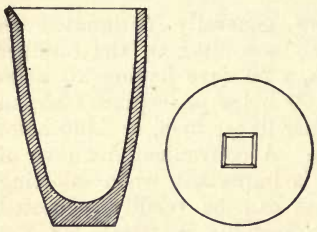

FIG. 81.

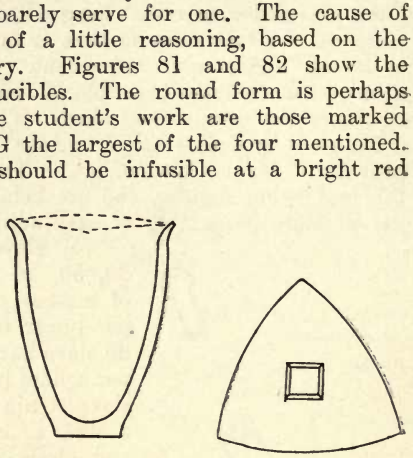

FIG. 82.

heat: test a chip for half an hour in a strong fire; the edges should not be rounded. It should also stand sudden changes of temperature: test by sudden heating and cooling. It should also be not too permeable: test by filling with water, and comparing the rate of permeability with that of a good crucible.

Circular lids are provided for the round crucibles, and triangular lids for the triangular form.

French Clay or French Crucibles.—These are more expensive than the ordinary "Clay" variety, and are excellent for the fusion of charges which can be poured. They are manufactured from a mixture of Paris clay and fine sand, and are frequently termed 'fluxing-pots.'

Both the "French" and the ordinary "Clay" crucibles may be obtained in a special form suitable for muffle fusions (Colorado crucibles).

The Hessian Crucible is manufactured from a mixture of three parts German clay and one part sand.

The Graphite Crucible in composition consists approximately of a mixture of one to seven parts of clay with three to ten parts of graphite. This crucible will be found serviceable for the fusion of certain metals and alloys. Strong oxidisers must be added sparingly, if at all, to charges in these crucibles.

Many other kinds and shapes of crucible will be found described in the various text-books on assaying.

Roasting Dishes.—Figure 83 shows in section the form most used. A convenient diameter is from 8 to 12 cm., according to the amount of ore to be roasted. They are usually made from the same clay as crucibles. For roasting quantities greater than 50 grams, iron dishes on top of the wind furnace, if carefully used, are satisfactory.

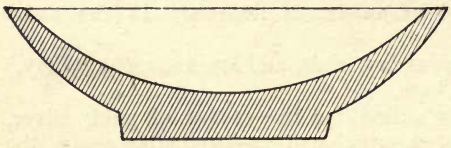

FIG. 83.

Scorifiers.—Figure 84 shows in section a form commonly used. The material here, again, is a refractory

clay. For general work the most convenient diameters are 5, 7, and 10 cm., but for small tests such as the student may wish to perform, 2·5 cm. scorifiers are suitable, taking up little room in the muffle.

It will be noticed that the bottom of the scorifier is thickened. Even with this, ores will be encountered occasionally that corrode completely through between the sides and base.

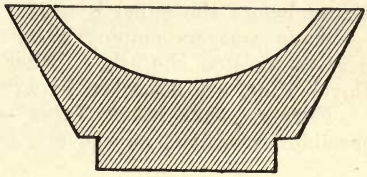

FIG. 84.

Muffles.—These are made either of refractory clay or of a mixture of clay and graphite. Those made from clay alone, with care, will be found to answer well. Figure 85 shows the shape commonly adopted.

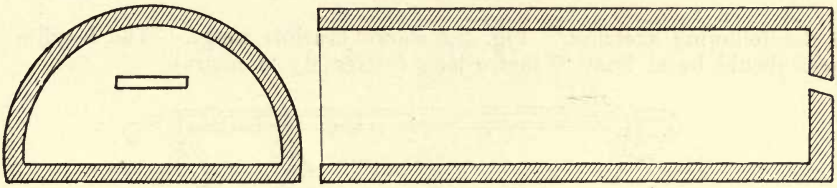

FIG. 85.

The "Colorado" muffle is specially designed to receive crucibles, and in section resembles a D lying on its side.

Cupel Moulds and Cupels.—Cupels known as "French Cupels" may be obtained ready for use in boxes of 100 or 144. The student, however, should make his own cupels; in some cases he may even have to prepare bone ash, though this can usually be obtained sufficiently pure.

Figure 86 shows the French cupel, and figure 87 an ordinary form. It is advisable that the upper inner edge of the cupel should be rounded as in *a*, fig. 88, and not sharp as at *b*. This prevents portions of a large button from catching on the sides. To manufacture cupels, moulds are necessary, and convenient diameters will be 1·8 cm. (for bullion), 2·5 and 3 cm. (for ores). Where a large number of cupels is daily required, it is advisable to procure a small machine; some of the machines recently designed in America rapidly turn out excellent cupels. Full instructions for the operation of these machines are supplied by the makers.

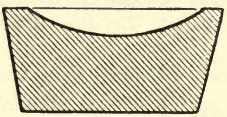

FIG. 86.

FIG. 87.

To make cupels, the mould is thoroughly cleaned; a few pounds of good bone ash are placed in a large tin basin, and water is gently sprinkled over the bone ash, which is at the same time continually stirred. This is continued till the bone ash on being squeezed firmly in the hand just adheres in a lump. The general tendency of beginners is to add too much water, which produces, on drying, a cupel hard as a brick. On rubbing the edge of a dry cupel it should just crumble slightly. Experience alone will teach the right proportion of moisture. The moistened bone ash is placed (not packed) into the mould, the piston is inserted, and several sharp blows are struck with a hammer or mallet. The cupel is then care-

FIG. 88.

fully removed and set aside in a warm place to dry. Several weeks should elapse before the cupel is used.

Some assayers employ a solution of "pearl ash" in water, others stale beer to moisten the ash. Other forms of moulds, such as those used at the Royal Mint, are described in advanced text-books.

Furnace and other Tools. — A set of tongs is necessary for handling crucibles, scorifiers, cupels, etc. in the furnaces. Convenient forms are shown

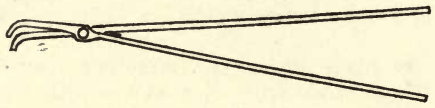

FIG. 89.

in the following sketches. Fig. 89 shows crucible tongs. The handles of these should be at least ·6 metre long (preferably ·8 metre).

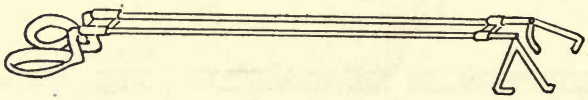

FIG. 90.

Figs. 90 and 91 show scorifier and cupel tongs, the handles of which, for comfort, should be at least ·8 metre long.

FIG. 91.

Pokers, scrapers for cleaning out muffles, stirrers for roasting dishes, shovels for coke and coal, cold chisels, etc. etc. are required, besides other odds and ends that want of space forbids mentioning.

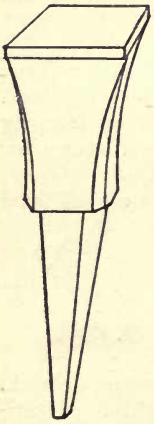

FIG. 92.

Two anvils will be necessary—a block of cast iron (an old die will do) or a small blacksmith's anvil, and a smaller anvil for fine work. This fine anvil must have a smooth polished face. Fig. 92 shows a convenient form.

Two hammers are necessary, one for rough work such as breaking slag, coke, etc., the other for fine work such as flattening beads, etc. Fig. 93 shows convenient shapes. The small light hammers sometimes supplied for this purpose should be avoided.

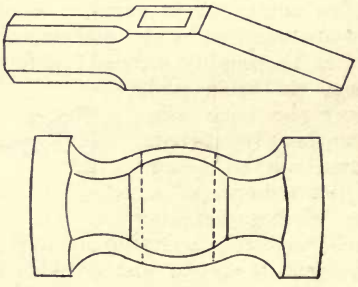

FIG. 93.

Moulds. — Ingot and slag moulds will also be required in addition to the foregoing.

Besides these articles there are many conveniences, such as cutting pliers, cupel trays, forceps, etc. etc., which the assayer

will procure as occasion demands. Complete lists of requisites will be found in the text-books on Assaying.

If the assay of gold and silver bullion is to be undertaken, a set of rolls must be added to the equipment. If much of this work is to be done it is advisable that a *good* set of rolls be procured at the outset. Those with the adjustment of the pressure regulated by *one* screw are preferable. Fig. 94 shows the "Braun" cornet rolls, which have positive feed, delivery and feed plates, and other improvements of use to the assayer.

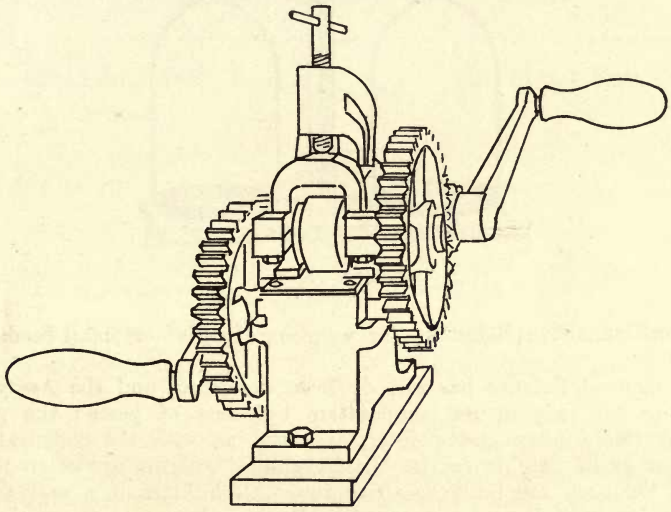

FIG. 94.

Chemical Apparatus. — A certain amount of chemical apparatus is required in connection with fire-work. The following list includes the more important requirements in this direction :— Porcelain capsules, royal Berlin (2·5 c.m. diameter) filter funnels, stand, beakers, filter paper, retort stand, bunsen or other burners, wash bottle, etc. ; also a small set of blowpipe apparatus, and the necessary reagents.

BALANCES, WEIGHTS, ETC.

In fire-assaying it will be found convenient to use three balances of varying ranges and degrees of accuracy.

(*a*) **Balances for coarse weighing.**—These are not absolutely essential, but will be found convenient for weighing out quantities of several pounds at one weighing. A range of one ounce to ten or twenty pounds will answer well. This balance may be conveniently replaced by 'spring' scales, which, however, should be checked now and then against standard weights.

(*b*) **Ore Balances of some accuracy.** — These are generally termed 'pulp scales,' and should be sensitive to one-tenth of a grain (or one centigramme), with a range of 1000 grains to $\frac{1}{10}$th grain (or 100 grammes to $\frac{1}{100}$th gramme). These balances are sufficiently delicate for weighing quantities of ore from 10 to 1000 grains. The student should note the degree of accuracy here attained ; *e.g.* if 400 grains of ore be weighed on such a balance, assuming the weights to be correct, then, as the balance is sensitive to $\frac{1}{10}$th of a grain, the error introduced cannot be greater than $\frac{1}{10}$th

in 400, or 1 in 4000. That is, the result of an assay cannot err more than $\frac{1}{4000}$th on the plus or minus side. Other errors will occur in the various operations, and these the student should as far as possible ascertain. The algebraic sum of these errors gives the total error.

A pair of pulp scales should be provided, with knife edges, levelling screws, level or plumb-bob and movable pans. Fig. 95 shows a suitable design.

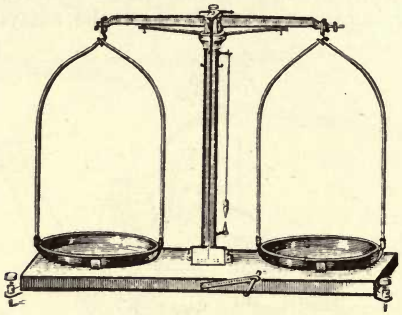

FIG. 95.

(*c*) **More sensitive Balances**, for weighing 'prills' or small beads of silver and gold.

The Chemical Balance has already been described, and the Assay Balance differs from it chiefly in its comparative lightness of parts; the graduated beam and rider, index and pointer, are read as with the chemical balance, except that grain weights or the 'half gramme' weights are often used.

Assay Balances are built sensitive to $\frac{1}{200}$th milligramme, and even more delicate still if specially ordered, but for all general work such as the student will perform a balance sensitive to $\frac{1}{20}$th of a milligramme answers excellently. Using the 'ten-grain' set of weights, the balance 'answers' to 0·001 grain, and using the 'half-gramme' set it 'answers' to 0·0001 of $\frac{1}{2}$ gramme, or $\frac{1}{20}$th of one milligramme. Thus, if using an 'assay ton' set of weights based on the 2000 lb. ton, if 1 milligramme represents (see Weights) 1 ounce per ton, the balance is read directly to $\frac{1}{20}$th milligramme, that is, to 1 dwt. By the use of special riders or by the methods of weighing previously given the student will see that further accuracy may readily be obtained.

The instructions previously given regarding the care of the balance apply again here. **Care** and **cleanliness** are absolutely essential to good work. This last sentence is reiterated for the benefit of the few students in most laboratories who adhere to the practice of placing cupels on the ledge of the balance; or, again, of handling delicate scale-pans with moist fingers. Such students should mend their ways, or be refused entrance to the balance room.

Weights.—In quantitative chemical analysis the 'gramme' system has so far been adhered to, and as far as the work of the student in the laboratory is concerned may still be retained; but the fire-assayer finds that in practice he is confronted with 'long tons,' 'round tons,' and other standards, and that he may have to discard the perfect metrical for a non-metric or a hybrid system. In Great Britain and her Colonies quantities of ore are estimated on the 'ton' unit; the ton generally equals 2240 lbs. avoirdupois—sometimes, but rarely, 2000 lbs. av. Quantities of gold and silver are estimated on the 'troy ounce' unit—two conflicting systems, with absolutely no rational basis.

Rationally, the ton should be replaced by the metric unit of 1000 'kilos' (=2203 lbs. approx.), the pound being replaced by the 'kilo' (=2 lbs. 3¼ oz.).

Weights of gold and silver will be represented in grammes and fractions of grammes.

The present disjointed system still holds sway, and the assayer compromises and makes the best of a bad job by adopting an 'assay ton' system. Some prejudice still exists against this method, but even a biased critic will find, on giving it a fair trial, that it is a rational labour-saving device.

According to the unit adopted—whether the 'long' ton of 2240 lbs. or the 'short' or 'round' ton of 2000 lbs.—two systems of 'assay ton' weights are in use. The following tabulation shows their relationship:—

The Long Ton. *British.*	**The Short Ton.** *American.*
1 Ton = 2240 lbs. av.	1 Ton = 2000 lbs. av.
1 lb. = 7000 troy grains.	1 lb. = 7000 troy grains.
1 Ton = 15,680,000 troy grains. **= 32,666 troy ounces.**	**1 Ton = 14,000,000 troy grains.** **= 29,166 troy ounces.**
Then **one Assay Ton** (A.T.) is made equal to **32,666 milligrammes.**	Then **one Assay Ton** (A.T.) is made equal to **29,166 milligrammes.**
1 Long Ton : 1 Assay Ton (A.T.) = 1 ounce troy : 1 milligramme. *E.g.* One A.T. of ore on assay yields a bead of gold weighing 0·0002 grammes, that is, ·2 of a milligram ; *but* 1 mgm. = 1 troy oz. Therefore the ore contains 4 dwts. gold per Long Ton.	1 Short Ton : 1 Assay Ton (A.T.) = 1 ounce troy : 1 milligramme. *E.g.* One A.T. of ore on assay yields a bead of gold weighing 0·0015 grammes, that is, 1·5 milligrammes ; *but* 1 mgm. = 1 troy oz. Therefore the ore contains 1½ oz. gold per Short Ton.

If the ore be weighed out in the ordinary way with grain or gramme weights, the contents per ton can only be ascertained from the weight of the bead by a troublesome calculation, or by reference to a set of tables.

The advantage, then, of the Assay Ton system is that the contents per ton are obtained directly, that is, without the aid of calculation or tables. The set of A.T. weights should range from $\frac{1}{20}$th to 4 A.Ts.

If A.T. weights are not obtainable, the ordinary grain or gramme weights may be used. These weights will be serviceable for tin and lead ores, but for gold and silver they involve the use of calculation: *e.g.* 400 grains of ore give a bead of gold weighing 0·012 grains; what are the gold contents per ton? To avoid calculation, a table is drawn up on, say, a 400 grain basis, and giving the contents per ton corresponding to every $\frac{1}{1000}$th of a grain from ·001 to 1 grain. A similar table may be drawn up for gramme weights, or for any combination of weights (see advanced text-books on Assaying).

For gold bullion it is advisable that a special set of weights be secured, the unit being 'half a gramme' = 1000 fine, and ranging with the rider down to ·0001 of half a gramme.

A set based on a 'ten-grain' unit, and ranging to ·001 grain, may be used. Special care should be taken in checking the accuracy (relative) of gold bullion weights. The accuracy of the other weights in relation to the ton used should also be checked by the student before proceeding to weigh ore or 'beads.' The methods of checking have been given in Part II.

In certain cases the assayer may have to report the gold and silver contents of ores in percentages. To do this rapidly a table must be prepared on a 400-grain, 30-gram, or other basis, working out the percentage corresponding to each successive 0·001 grain, or 0·0001 gram, as indicated in the following :—

Ore taken.	Gold found.	Percentage.
400 grains	0·001 grain.	·00025%
,,	0·002 ,,	·0005%
,,	0·003 ,,	·00075%
	etc.	etc.

CHAPTER IV.

MANIPULATION.

THE fire-assayer will repeatedly have to perform the operations of **Reduction, Sampling, Estimation** of **Moisture, Calcination, Roasting, Fusion, Scorification, Cupellation, Inquartation** and **Parting, Weighing** and **Calculations** of **Results.**

To simplify future descriptions of methods, these operations will now be treated in detail, and only such additional observations will then be made as the peculiar nature of any modified operation may require.

Sampling and Reduction.

The student must always bear in mind that the aim he has in view is to ascertain as accurately as possible (consistent with fair speed) the gold, silver or other contents of a quantity of ore, and that to do this

(1) *The ore must be accurately sampled.*
(2) *The sample obtained must be accurately assayed.*

It is clearly evident that several tons of ore cannot be treated in a crucible in the assay furnace, and that, if an average sample of the 'parcel' be obtained, and from it, again, an average sample of 1 A.T. be selected, then from the results of an accurate assay the contents of the 'parcel' may easily be calculated.

The student must therefore exercise every care in the selection of this sample; for however accurate the assay may be, the results are valueless if the sampling be inaccurate; and in the majority of disputes regarding assay results, it will be found that inaccurate sampling has caused the discrepancy, not inaccurate assaying.

Further, the student must both before, during, and after taking his sample take every precaution that the sample obtained has not been tampered with in any way. Where monetary considerations come into play, the assayer, as a matter of duty, should consider the possibility and probability of his samples being 'salted,' and take precautions accordingly.

It is not within the scope of a work of this nature to discuss the sampling of 'ore veins' and the keeping of assay plans of mines; for information on these points the student is referred to more advanced text-books, and to Hatch and Chalmers or Truscott on the Witwatersrand gold fields. Here it is assumed that the ore in a coarse state lies ready for sampling, or that the assayer is called upon to sample a heap of tailings or other material.

The method of sampling and reduction depends largely on the nature and

quantity of the material to be sampled. If a large quantity of ore in coarse lumps has to be dealt with, hand sampling should be replaced by machinery, arranged to work automatically. Such machinery should be so designed that it may be readily and thoroughly cleaned, and generally consists of coarse and fine stone crushers, rolls, and sampler, arranged automatically and set to deliver a constant sample, bearing a definite ratio to the total ore crushed. For details of these appliances see *Copper Smelting*, by Peters, and other metallurgical literature.

To take a concrete case and one that is more within the reach of the student than the previous, it will be assumed that the student is confronted with a parcel of ore weighing one or two hundredweights, and consisting of pieces of ore up to about six inches in diameter.

(1) By the aid of the 'sledge' reduce the larger pieces to a diameter of about two inches, and from the heap of ore carefully select about one-twentieth, thus obtaining a sample of about 10 or 12 lbs. weight. Care must be taken that any 'fine' material is also carefully collected and sampled.

(2) In a small rock-breaker or mortar reduce this sample to pieces about one quarter to one half inch in diameter. Again carefully sample, selecting this time about one-eighth or one-tenth, thus obtaining a sample of about one pound.

(3) Reduce this latter sample by aid of mortar and bucking-plate till it is passed through an 80 sieve. Gather the sifted ore into a flat pyramid after careful and thorough mixing; flatten further the pyramid and quarter it with a spatula; reject any two opposite quarters; collect the remaining quarters and repeat on them the mixing and quartering, and about 1500 grains will be left.

(4) Spread the 1500 grains of ore on a sheet of glazed paper. Mix well and flatten out the ore to about one quarter inch in depth. The assay sample may now be taken by carefully selecting here and there with the spatula small quantities of ore.

The above process may be carried out by repeated quarterings. To reduce 2 cwt. to $1\frac{3}{4}$ lb. requires seven quarterings; a tedious process. Probably the best method consistent with both speed and accuracy is to quarter; then select from each quarter a quarter, thus obtaining 4 portions each $\frac{1}{16}$ of the original. Reduce and repeat, and one-sixteenth of the original, that is 16 lbs., remains; repeat, and 4 lbs. remain; repeat, and 1 lb. is left, which is treated as before.

When the ore is contained in a bag, box, or other receptacle, the *entire* contents must be emptied out before commencing sampling.

It may be found on sifting or it may be noticed beforehand that the ore contains **metallic particles**. If these, on grinding, refuse to pass readily through the sieve, a larger lot must be selected, say about two pounds. More care must be exercised throughout in the thorough mixing and sampling at each stage. The 2 lbs. of ore are ground fine and sifted till two portions are obtained—

(a) Metallic particles.

(b) Sifted ore.

Weigh each portion. The metallic particles will be estimated as a whole, and the total gold contained calculated back to the total ore $(a+b)$. The sifted ore is treated as usual and calculated back to the total $(a+b)$; by combining the two results the value is obtained. (See "*Calculation of Results.*")

For details regarding the sampling of residues in cyanide vats, tailings,

pits and dams, ore bags, bullion, etc. etc., consult the following pages and the more advanced text-books on Assaying and Metallurgy.

The student at every point in the operation of sampling must bear in mind that he is endeavouring to obtain an average sample. He must often depend on his judgment, which can only be ripened by experience, and at the same time he must discard the personal element and aim at the impartial operation of the ideal sampling machine.

The student will find an excellent discussion on the Theory of Sampling in the Appendix C to *Beringer's Assaying*. In practice, Beringer gives the following scale of reduction in stages A to D, etc.:—

A = 1000 tons rocks and lumps of ore.
B = 50 ,, rough stones ($\frac{1}{20}$th size lumps in A).
C = 2·5 ,, small stones ($\frac{1}{20}$th ,, stones in B).
D = ·125 ,, coarse powder ($\frac{1}{20}$th ,, small stones in C).

At each stage this is a 5% reduction, accompanied by a corresponding decrease in the size of particle, the number of particles remaining the same.

In 'quartering' 64 pieces of stone we select two opposite quarters, that is 32 pieces, that is half the sample. Before the next quartering (really halving) each one of these 32 pieces should be broken into two, and so the process goes on till the ore passes through the required mesh; therefore we have a final sample of 32 minute particles—a sample much too small. A much larger initial number of pieces must be taken, or the rate of reduction must be altered. This latter course is roughly adopted in practice; the 64 pieces could each be broken into four, and so on, the number of particles in the sample being doubled at each operation. As the assayer cannot obtain what may be called a mathematically exact sample, he must direct his energies to approach as nearly as possible this ideal. The student on sampling a heap should give one-half to a fellow student, and compare the results of the assays. The comparison will be both interesting and useful.

Moisture Estimation, Drying, etc.

In estimating the value of ores, the amount of gold, silver, etc., per ton is required. Now, if a ton of thoroughly dry ore be exposed to a moist atmosphere for several days it will be found to have increased in weight; that is, it has absorbed a certain amount of moisture. This amount of moisture is found in practice to be very variable, hence it is necessary that the moisture in an ore be estimated and the value stated in terms of dry ore.

The student should distinguish clearly between the terms *Drying*, *Calcination*, and *Roasting*.

Drying signifies the expulsion of moisture.

Calcination signifies the expulsion of CO_2 and other volatile constituents.

Roasting involves a chemical change, with the addition of an element.

In Part II. the estimation of H_2O in dolomite has been described. The student now has to estimate the moisture in a parcel of ore. This may be done approximately by weighing out 400 grams of moist ore in an iron pan, and drying in an oven till moisture ceases rising from the surface. Cool and reweigh.

Original weight	dish + 400 gm. ore,	450 gm.
Final ,,	,, + ore less moisture	410 ,,
	Moisture,	40 ,,

That is, 10% of moisture, or 400 grams moist ore, are equivalent, as far as metal contents go, to 360 grams dry ore.

The following method will give more accurate results:—

The temperature most suitable for drying ranges between 100° C. and 120° C. To adopt a uniform standard the water bath may be adopted, or the air bath with the regulator set at 100° C. Although this temperature may not be sufficiently high to drive out the last traces of moisture, yet it forms a convenient standard to which all assays may be referred. 100 grams of ore are weighed out and transferred to a shallow porcelain basin, which is then placed in the water or air oven, and there allowed to remain for one hour; cool and reweigh. Place again in the oven for half an hour; cool and reweigh, and repeat till constant. The total time of operation depends on the percentage of moisture and the nature of the ore. In some works where ores are bought it is the custom for buyer and seller to select, in the evening, moisture samples, which are placed in ovens in a fume chamber, the door of which is then closed and sealed. In the morning, when both parties are present, the seals are broken, the samples cooled and reweighed, and then removed for assay.

In practice the assayer should base all his estimations on the dried ore, and where necessary he will, on receipt of the ore, conduct a moisture estimation. To be of any use this must be performed at once, as the ore will likely become more dry in the atmosphere of the assay office. The student must remember that to get concordant results on a number of assays of one ore the dried ore should be used, and if sometime elapses (say one or two days) between successive assays, the ore should be redried for a short period before using a second time.

Calcination.—As CO_2 and other volatile substances have to be removed, a much higher temperature is required than in the operation of drying. In calcining, as in drying, it is not necessary that the air should have free access; it is only necessary that the temperature be sufficiently high to drive off the volatile substances, and in many cases a red to white heat will be found necessary. Instead of iron dishes, fireclay roasting dishes may be used. The substance to be calcined is subjected to a red heat, the temperature being gradually raised until the volatile constituents are nearly all expelled. This may be checked either by weighing or by chemical or other tests. Limestone is a convenient substance for the student to operate on.

Roasting.—As the assayer will be frequently called upon to perform this operation, he should thoroughly master both the theory underlying the process and the necessary manipulation.

On heating **iron pyrites** (FeS_2) in a current of air, the following reactions take place:—

(1) At a *low red* moisture is expelled, and one atom of Sulphur in FeS_2 is volatilised and oxidised to form SO_2. This reaction requires the presence of oxygen, and is most vigorous on the surface of the charge. Till the disappearance of the pale blue flame the gases produced are steam and SO_2.

(2) A second stage commences: the iron and the second atom of sulphur begin to be oxidised. A certain amount of SO_3 is now formed. FeO is formed, and a portion of this oxide unites with SO_3, forming $FeSO_4$ (can be detected by solubility in water). This $FeSO_4$ breaks up into $FeO + SO_2 + O$, and acts as a powerful oxidiser; and FeO is converted into Fe_2O_3, a fairly stable oxide (see details, p. 240).

If **other sulphides** be present, this SO_2 and O aid in oxidising them to sulphates, and before the complete decomposition of the $FeSO_4$ any **copper pyrites**, if present, is oxidised, $FeSO_4$ and $CuSO_4$ being formed (apply tests).

(3) *Raise the Temperature.*—The $CuSO_4$ changes to a basic sulphate, then to a

dioxide, and then to a monoxide, these last changes requiring a high temperature and much time. The oxidation of the Fe is complete when the maximum of $CuSO_4$ is formed.

If **Silver** be present Ag_2SO_4 begins to form when 75% of the $CuSO_4$ is decomposed, and the formation proceeds rapidly when once started. The maximum occurs when all the $CuSO_4$ is decomposed. Prolonged treatment at a high temperature is required to break up Ag_2SO_4.

If **Galena** be present $PbSO_4$ is formed, which is partially changed to PbO, resulting in a mixture of sulphate and oxide.

If **Zinc Blende** be present a higher heat still is required, and a certain amount of basic sulphate always remains.

If **Calcite** be present it is converted into $CaSO_4$.

If **Arsenic** and **Antimony** be present they are partially volatilised and partly converted into arsenates and antimoniates. To break up these, charcoal powder should be added, when nearly all the sulphates are decomposed; the heat raised and the charge stirred.

Practical Hints.—(1) If much PbS or Sb_2S_3 be present add to the charge ½ part of fine *clean* sand (prevents caking).

(2) To ores containing As or Sb add ½ part of charcoal *finely* powdered (reduces As and Sb compounds).

(3) To ores containing over 60% of sulphides add ¼ to ½ part fine sand (prevents caking).

(4) Begin the 'roast' at a low temperature—a very dull red; when the blue flame appears, stir every few minutes. The ore begins to glow. Stir till the glowing ceases and the ore appears uniform in colour. Ammonia carbonate is sometimes used with ores containing Cu, As, and Sb. It converts any SO_4 to $(NH_4)_2SO_4$ which is volatile, hence at the outset a very low heat must be used until all ammonia fumes are driven off.

Fusion.

A perfect fusion should result in a complete separation of the valuable metal from the 'gangue' or worthless materials. This involves certain favourable conditions—

(1) Suitable fluxes must be added to form a liquid slag. If the slag be viscous it is apt to retain small prills of metal. The nature of the various fluxes used has already been discussed, and the student will find further instructions regarding the choice of fluxes when the various methods of assay are detailed.

(2) When the metals sought are present in very small quantities (*e.g.* gold or silver in an ore assaying 1 to 100 ounces), it is necessary that a 'collecting' agent be used to dissolve the tiny particles of gold and silver.

(3) That the temperature of the fire be properly controlled.

(4) That the time of fusion be neither too short nor too long.

Conditions (1) and (2) will not be considered in this place.

Re condition (3).—**The Temperature of the Fire.**—This will generally be stated as dull red, red, bright red, or white. Experience will guide the student in distinguishing these different temperatures. It is essential to the proper control of the temperature that the furnace be under control, and to this end a damper in the flue or on the ash box will be necessary. By the manipulation of this and careful stoking the student with practice will be able to command a fair range of temperatures.

To obtain good work the coke or other fuel used should be broken into small pieces of uniform size. For a dull red to a bright red fire the pieces should be approximately one inch in diameter; for a bright red to a white

heat, about one and a half inches. A sieve with $\frac{3}{4}''$ meshes will be convenient, all siftings being rejected. In building up a fire, if a high heat be required at the outset, 'dummies,' that is, old crucibles, should be built in, and when the heat is strong enough they are removed and the assays introduced in the cavities left.

Re condition (4).—**Time of Fusion.** — When each assay is considered in detail the time of fusion will be stated. Unfortunately sufficient attention does not hitherto seem to have been given to this point; *e.g.* in the KCN estimation of tin authorities give the following—

Beringer,	3 to 6 minutes
Brown and Griffiths,	15 minutes
Aaron,	5 minutes after fusion
Ricketts and Miller	30 minutes

That is, a variation of 3 to 30 minutes. As all these authorities claim good results, the student can only conclude that the time of fusion admits of variation, and that continuous practice on any of these methods will bring good results.

Scorification.

By this is meant the subjection at a high temperature to an oxidising atmosphere of a charge of ore mixed with certain reagents. The following conditions are essential to scorification—

(1) That the charge be mixed with such reagents as will produce a fluid slag and at the same time collect the precious metals into a button.

(2) That a 'muffle furnace' be used, the temperature of which can be regulated from almost a white heat down to a dull red.

(3) That a sufficient supply of oxygen be available to oxidise lead to litharge.

Condition (1).—The chief reagent used in scorification is granulated lead, which acts in two ways: (*a*) as a 'collectant' for gold and silver, and (*b*) by oxidation to litharge it acts as a flux, forming with siliceous matter fusible silicates of lead. Borax glass (borax fused in a crucible, poured, cooled, and ground fine) is also largely used; this unites with oxides, and aided by the litharge forms fusible liquid slags.

Silica, charcoal, iron, and 'soda' are occasionally used as reagents—silica and soda as fluxes, charcoal as a reducer, and iron as a desulphuriser.

Condition (2).—Sketches have already been given of the "muffle" and "muffle furnace." The student will find that the regulation of the temperature requires careful stoking and manipulation of the draught. If using a 'top-feed muffle' (see fig. 77) the coke should be carefully broken to inch lumps and all finer material rejected. The fire should not be allowed to fall too low before restoking or the muffle will be chilled, thus endangering any assays it may contain. With an 'under-fed' muffle (see fig. 78) the size of the coal or coke may be from one to two inch pieces. The necessary temperatures will be mentioned when the actual assay is described.

Condition (3).—The presence of oxygen is absolutely essential. The rate of oxidation may be regulated by the muffle doors, which may be opened or closed. The muffle should always be provided with a slot or slots (hole or holes) in the end or sides; without these the action will be extremely slow. Some of the more modern muffle furnaces are provided with a flue leading from the back of the muffle. A damper in this flue permits the easy adjustment of the draught of air through the muffle.

Practical Hints.—(1) See that suitable proportions of reagents are mixed with the ore. (See Charges.)

(2) As a general rule, unless a special preliminary roasting be advised,

the muffle should be at a *bright red* heat before introducing the scorifier and charge.

(3) After introduction close all doors for 3 to 5 minutes till the lead is liquid.

(4) When the lead is perfectly liquid open the doors; a roasting process now commences, As, Sb, S, etc., volatilising, oxides of metals being formed. A slag gradually forms from the borax litharge (oxidised lead), metallic oxides, and any silica present.

(5) When the 'eye' formed by the slag closes in to about $\frac{1}{4}''$ in diameter, raise the temperature for a few minutes and then pour the charge.

(6) If the scorifier be much corroded add some silica to the next charge.

(7) In certain cases, for example, with ores containing arsenic and antimony, a crust may form on the surface; by a slight touch with the point of a bent wire the molten lead may be exposed. The addition of some powdered charcoal will assist the process.

From the foregoing notes the student will see that the so-called '**scorification**' of an ore is not a simple operation, but consists of four processes:—

(1) **Melting.**—A strong heat for a few minutes melts the lead.

(2) **Roasting.**—The ore floats on the lead and is partially roasted.

(3) **Fusion.**—Fumes of SO_2, etc. cease rising and the ore disappears. Fusion of the ore proceeds; a higher temperature is now required.

(4) **Scorification proper.**—A uniform temperature is now maintained. The ring of slag formed gradually closes in.

The student in conducting the operations subsequently detailed should note these four stages. The scorification of an ore requires care; it is not sufficient simply to place the scorifier and charge in the muffle and then leave the assay to its fate. With some ores fairly accurate results may be obtained by this careless treatment, for which no thanks are due to the skill of the assayer, but with other ores only careful attention to all details can give satisfactory results.

Cupellation.

By this term is meant the separation of gold and silver from an alloy of gold, silver, and lead, by exposing the alloy in a bone ash vessel to a red heat in an oxidising atmosphere.

A perfect separation of the gold and silver from the lead is under ordinary conditions rarely, if ever, attained, yet with care and the use of 'checks' (see Checks) a high degree of accuracy may be attained, the following conditions being necessary:—

(1) That the cupel be neither too hard nor too soft, its surface being neither too rough nor too smoth, and that it be thoroughly dried before use.

(2) That the button be clean, that is, 'not brittle.' Certain impurities prevent successful cupellation.

(3) That the temperature of the muffle furnace be regulated from a 'red' to a 'bright red' heat, that is, it should not be 'dull red' nor 'white.'

Condition (1).—The manufacture of cupels has already been described, but it is difficult to define what is meant by the phrases "too soft," "too hard," etc. Concerning such points the student will learn more by practice and close observation than from pages of description. It is advisable in preparing cupels for 'bullion' work to sprinkle on top of the bone ash in the mould a thin layer of sifted bone ash. If the texture of the cupel be too coarse, there is danger of loss through too rapid saturation of the litharge into the cupel; if too close, the saturation is too slow and scorification takes place, rendering the process slow and uncertain.

Condition (2).—The student will know either from preliminary tests or, in

some cases, from the appearance of the button, whether or no it is suitable for cupellation. As will be seen further on, copper, if present to a certain extent, can be removed by repeated additions of lead during the cupellation. When a button is brittle owing to the presence of S, Sb, etc., it will not cupel successfully without a preliminary scorification.

When carrying out the practical instructions given in Chapter VI., the student will gain an insight into the effects of certain impurities in the button. He should also notice, when assaying bullion, the effect of varying quantities of copper in the bullion, the shape of the button after cupellation, the manner in which it adheres to the cupel, etc.

Condition (3).—Special attention must be paid to the temperature of the muffle, more espccially when dealing with a button containing silver. In Chapter VI. the student is instructed to perform certain experiments to determine the loss of silver by volatilisation. He will find that certain conditions of temperature are necessary to minimise this loss.

Practical Hints.—(1) Select a good dry cupel about one-fourth heavier than the button.

(2) Heat the muffle to a bright red and stoke well.

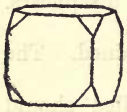

Fig. 96.

(3) Insert the cupel for 5 minutes; examine for any cracks.

(4) Flatten the corners of the cubical button as in fig. 96, and insert it into the cupel.

(5) Close the doors for a few minutes till the button fuses and the dark coating disappears.

(6) Reduce the temperature slightly till a ring of litharge flakes ('feathers') just appears (open the doors).

(7) Maintain this temperature till the button ceases diminishing and suddenly flashes.

(8) Now close the doors for one or two minutes to remove the last traces of lead.

(9) If the button contain much silver (over 60%) remove the cupel gradually from the muffle, or cover it with a red-hot cupel and remove at once. Slow cooling is necessary to prevent the bead sprouting (due probably to sudden evolution of occluded oxygen).

The student will notice three main stages during cupellation:—

(1) *Melting the button.*

(2) *Cupellation proper;* the oxidation of the lead to litharge, part of which passes off as fumes and part is absorbed into the cupel.

(3) *The finishing stage.* All the lead is now removed.

The above notes refer to the normal case of cupellation; but the student will probably meet with some of the following difficulties:—

Freezing or solidification of the button, caused either by the presence of infusible substances or by the temperature being too low. In the first case the button should have been scorified, and in the second case the heat must be raised. The addition of a little lead and the introduction of a few pieces of charcoal to raise the temperature often effect a cure. Result rather unsatisfactory.

Scorification.—Here a ring of litharge is seen floating round the lead button, the cause being too dense a cupel or too rapid formation of PbO. In the first case procure good cupels; in the second raise the temperature and add a pinch of powdered charcoal.

Spitting at the commencement of the cupellation is due either to a cold cupel or to the presence of As, Sb, S, etc. in the button. In the first case the cupel should be well heated before use; in the second, preliminary scorification is the remedy.

Several other minor difficulties, such as cracks in the cupel, etc., may arise; but it may be laid down as a rule that in such cases either the button requires preliminary scorification or the cupel is not up to the mark.

Inquartation and Parting.

By this is meant the adjustment of a certain relation between the gold and silver in a gold-silver alloy, and the separation of the silver from the gold by solution in acid. That this be successful two main conditions must be satisfied—

(1) A certain relationship as to quantity must exist between the gold and silver in the alloy.

(2) That the alloy, when this relationship exists, be treated with a certain acid of certain strength.

Condition (1).—The proportion of gold to silver is given as follows:—

	Gold.		Silver.
Brown & Griffiths, ...	1	:	2·5
Beringer, ...	1	:	2·5
Rose, ...	1	:	2
Ricketts and Miller (*New York Assay Office*),	1	:	2
Aaron, ...	1	:	2·5

Some variation exists in practice. When the ratio becomes 1 : 3 the flattened bead or cornet tends to break up, and when it rises to 1 : 8 the bead falls into powder on treatment with acid. Many assayers when estimating the gold in ores roughly add an excess of silver to the bead or ore, the ratio being anywhere between 1 : 3 and 1 : 8. For accurate bullion work, however, it is absolutely essential that the ratio range between 1 : 2 and 1 : 3. The student is recommended to choose the ratio 1 : 2·5.

It is necessary when adding silver to a bead to thoroughly melt the alloy. Too low a temperature will result in an uneven mixing of the gold and silver.

Condition (2).—The alloy must now be treated with an acid, and in order that the acid may have an opportunity of attacking the silver the bead is flattened with a hammer or passed through cornet rolls (see Bullion Assaying) till of a suitable thinness. The only attempt made at defining the thinness of a cornet is in the statement given, that the cornet is rolled till as thin as a visiting card—a somewhat variable dimension. Having flattened or rolled the alloy, it is transferred to the acid. For beads, small porcelain cups 2·5 c.m. in diameter answer best; for bullion, beakers or special platinum apparatus, where a number of assays are to be done. The strength of acid has been given (see Reagents); the time of treatment in the acid and the quantity and temperature of the acid will be given later on.

After treatment in the acid, the gold is washed, collected, dried, annealed, and then weighed.

Practical Hints.—(1) See that all apparatus—hammers, anvils, rolls, porcelain cups, beakers, etc.—are **thoroughly clean**, and that the necessary reagents are prepared according to instructions.

(2) When handling fine beads, never carry them any distance in the forceps. When, for example, a bead is to be transferred from a cupel to a porcelain crucible, the two are set side by side, and the bead transferred with the forceps.

(3) When flattening beads, use a moderately heavy hammer with a very slight convexity on its face. Whenever a bead shows signs of splitting, anneal it at once.

(4) Part small beads in a porcelain cup, using only one strength of acid (see Reagents). For bullion, use both strengths of acid at the temperatures directed.

(5) When washing the gold, carefully tap the small cup, and carefully decant the liquid down a glass rod into the 'waste' bottle.

(6) Gently dry the cup and gold on a hot plate or sand bath, and anneal with mouth blowpipe if a small bead, and in the muffle in an annealing cup if a cornet.

The student who has had a course of training in the manipulations of quantitative analysis will meet with little difficulty in parting gold from silver. Care is necessary in certain cases to prevent the loss of a few very small particles of gold. These generally sink with the application of a few drops of cold water from the wash bottle, or by a touch from a small glass rod. The chemistry of this process is simple. With the ratio of 1 Au. : 2·5 Ag. the gold forms a network, and permits the action of solution to progress steadily and completely.

Weighing.—The student who has performed the analytical operations in Part II. should now be able to weigh accurately and with fair rapidity; he will have little fresh to learn here, except that in many cases smaller quantities of material will have to be estimated by weight than previously. The balance used is more sensitive than before.

In weighing out fluxes a high degree of accuracy is not necessary; for a charge of 'soda' of, say, 600 grains, an error of 5 grains is immaterial; the weighing may be rapidly performed, roughly adding or removing the soda with a spatula or horn scoop till the *approximate* weight is obtained. The only substances requiring accurate weighing are the ore and the reducer, and this latter often requires no great accuracy. Many assayers simply measure by volume the litharge, soda, argol, and borax necessary; the student, however, is advised, for the first six months at least, to weigh all charges of fluxes, etc.

In weighing beads of gold or gold and silver the student may find that, in the case of very small beads, when using certain balances, he is unable to place the rider near the centre of the beam on account of the vane and screw. In such a case the bead may be weighed by placing the right-hand rider on the 4 mark, and with empty pans adjusting the left-hand rider till the riders exactly counterbalance. Add the bead to the left pan; now shift the r.h. rider to restore equilibrium.

> Weight bead in grains = observed weight on r.h. rider – ·040 (using grain weights).
> Similarly with gram weights (– ·0040).

When weighing 10 grains or ·5 gram bullion on a delicate balance, the student will find some difficulty in obtaining the exact weight (10·000 or ·5000). Continual practice is required to overcome this, but where the student has little time and does not intend specialising in bullion work, he is advised to weigh as near the required quantity as possible, then note the exact weight by using the rider, and then obtain his fineness by calculation, as follows:—

Instead of 10 grains the student has on the pan 9·994 grains bullion This latter weight he assays, obtaining 6·324 grains gold; therefore

$$9{\cdot}994 : 10 :: 6{\cdot}324 : \text{Fineness}$$

$$\frac{10 \times 6{\cdot}324}{9{\cdot}994} = \text{Fineness}$$

The slide rule is very convenient for such calculations.

The weights used have been described, and in practice the assayer will use the weights which give most directly the results in the form required by the management. In the course of this work the assay ton (short) will be adopted for ores, and the 'half gramme' (=1000) for bullion. For ores such as lead or tin, where the percentage of a metal is required, gramme weights will be used; the stndent, however, should have little difficulty in converting from one system to another.

Calculations and Reports.

The guiding rule here is that all reports be stated clearly and briefly, avoiding as far as possible technical terms and phrases.

The following tabulation shows the chief types of report that may be required, and the various weights that may be used to obtain the result in the required forms. Instead of dwts, grs. etc., decimal fractions of ounces may be used.

Form of Report.	Weights for Ore.	Weights for Gold.
Ounces, etc., per Long Ton.	1. A.T. (long).	Gramme.
	2. Grain.	Grain and Table A. Gramme ,, ,, B.
	3. Gramme.	Gramme ,, ,, C. Grain ,, ,, D.
Ounces, etc. per Short Ton.	1. A.T. (short).	Gramme.
	2. Grain.	Grain and Table E. Gramme ,, ,, F.
	3. Gramme.	Gramme ,, ,, G. Grain ,, ,, H.
Gold and Silver percentage.	Gramme. Grain.	Gramme and calculation. Grain ,, ,,
Other metals. ,,	Gramme. Grain.	Gramme ,, ,, Grain ,, ,,

Want of space prohibits the insertion of the complete tables, but from the sections given the student will find little difficulty in enlarging the tables to any extent.

Table A.

400 grs. ore give	One ton gives		
grains gold	oz.	dwt.	grs.
·001	0	1	15
·002	0	3	6
·003	0	4	21
·004	0	6	12
·005	0	8	4
·006	0	9	17
·007	0	11	10
·008	0	13	1
·009	0	14	16
·010	0	16	8
etc.	etc.	etc.	etc.

Table B.

400 grs. ore give	One ton gives		
grams gold	oz.	dwt.	grs.
·0001	0	2	12
·0002	0	5	1
·0003	0	7	13
·0004	0	10	2
·0005	0	12	14
·0006	0	15	0
·0007	0	17	15
·0008	1	0	4
·0009	1	2	16
·0010	1	5	5
etc.	etc.	etc.	etc.

Table C.

40 grams ore give	One ton gives		
grains gold	oz.	dwt.	grs.
·001	0	1	1·3
·002	0	2	2·6
·003	0	3	3·9
·004	0	4	5·2
·005	0	5	6·5
·006	0	6	7·8
·007	0	7	9·1
·008	0	8	10·11
·009	0	9	11·7
·010	0	10	13
etc.	etc.	etc.	etc.

Table D.

40 grams ore give	One ton gives		
grams gold	oz.	dwt.	grs.
·0001	0	1	14·9
·0002	0	3	5·8
·0003	0	4	10·7
·0004	0	6	11·1
·0005	0	8	2·5
·0006	0	9	17·4
·0007	0	11	8·3
·0008	0	12	23·2
·0009	0	14	14·1
·0010	0	16	5
etc.	etc.	etc.	etc.

Table E.

400 grains ore give	One ton gives		
grains	oz.	dwt.	grs.
·001	0	1	10·8
·002	0	2	21·6
·003	0	4	8·4
·004	0	5	19·2
·005	0	7	6
·006	0	8	16·8
·007	0	10	3·6
·008	0	11	14·4
·009	0	13	1·2
·010	0	14	12
etc.	etc.	etc.	etc.

Table F.

400 grains ore give	One ton gives		
grams	oz.	dwt.	grs.
·0001	0	2	5·5
·0002	0	4	11
·0003	0	6	16·5
·0004	0	8	22
·0005	0	11	3·5
·0006	0	13	9
·0007	0	15	14·5
·0008	0	17	20
·0009	1	0	1·5
·0010	1	2	7
etc.	etc.	etc.	etc.

Table G.

40 grams ore give	One ton gives		
grains gold	oz.	dwt.	grs.
·001	0	0	22·6
·002	0	1	21·2
·003	0	2	19·8
·004	0	3	18·4
·005	0	4	17
·006	0	5	15·6
·007	0	6	14·2
·008	0	7	12·8
·009	0	8	11·4
·010	0	9	10
etc.	etc.	etc.	etc.

Table H.

40 grams ore give	One ton gives		
grams gold	oz.	dwt.	grs.
·0001	0	1	10·7
·0002	0	2	21·4
·0003	0	4	8·1
·0004	0	5	18·8
·0005	0	7	5·5
·0006	0	8	16·2
·0007	0	10	2·9
·0008	0	11	13·6
·0009	0	13	0·3
·0010	0	14	11·0
etc.	etc.	etc.	etc.

The use of these tables is self-evident, the weight of the bead being found in the first column, and the value in oz., dwt., grs. per ton in the second column. If, for example, instead of taking 400 grains of ore 600 be taken, and the bead weighs ·009 grains, then 400 grains would give ·006 grains, which from Table A is found to correspond to 9 dwt. 17 grains.

The following table will be found convenient for conversions from A.T. to grams and grains:—

ASSAY TONS IN GRAMS AND GRAINS.

A.T. (short).	Grams.	Grains.
0·1	2·916	45·009
0·2	5·833	90·019
0·3	8·749	135·029
0·4	11·666	180·039
0·5	14·583	225·049
0·6	17·499	270·059
0·7	20·416	315·069
0·8	23·333	360·079
0·9	26·249	405·089
1·0	29·166	450·099

By the aid of this table the student may convert the A.T. weights of ore, flux, etc. in the following pages into grams or grains if A.T. weights be not obtainable.

When estimating the value of an ore containing metallic scales the calculation is made as follows—

Ore taken, 10 A.Ts. A.
Siftings, $9\frac{4}{5}$ A.T. B.
Scales, $\frac{1}{20}$ A.T. C.
} A little ore may be lost in sifting.

Sifted Ore B. 1 A.T. by assay yielded 1·2 mgms. gold.

∴ Total gold in siftings = 1·2 × 9·8.
= 11·76 mgms.

Scales C.—Scorified with lead, cupelled and parted, gave ·6321 grams or 632·1 mgms. gold.

∴ Total gold in Scales = 632·1 mgms.

∴ **Total gold in A**
= Gold in B + Gold in C.

Total gold in 10 A.Ts. ore
= 11·76 + 632·1 mgms.
= 643·86 mgms.

Total Gold in 1 A.T. ore
= 64·386 mgms.

Gold in ore = 64·386 oz. per ton
= 64 oz. 7 dwt. 17 grs.

The silver may be estimated in a similar manner. It will be found convenient to subdivide the $\frac{1}{20}$ A.T. weight into $\frac{1}{50} + \frac{1}{50} + \frac{1}{100}$ (·05 A.T. = ·02 A.T. + ·02 A.T. + ·01 A.T.). The scales may then be accurately weighed and the calculation performed with A.T. weights as shown above.

A somewhat similar though more complicated calculation is necessary if gram or grain weights be used.

CHAPTER V.

PRELIMINARY EXAMINATION OF ORES.

By this time the student should be competent in general qualitative analysis, and he will now be able to apply his knowledge where necessary and the student who has advanced so far in mineralogy as to be able to distinguish some fifty of the commoner minerals will have little difficulty in obtaining a fair idea as to the contents of any ore.

Generally, it is not necessary that a preliminary examination be exhaustive, the presence or absence of some few elements or compounds being all that is sought for. Such preliminary examination may be carried out by

(1) **Inspection alone.**
(2) **Dry tests alone, or aided by inspection.**
(3) **Wet Tests alone, or aided by inspection and dry tests.**

(1) **Inspection alone.**—The experienced assayer or the mineralogical student will in many cases require no other aid than mere inspection, accompanied, if needful, by the usual physical tests of hardness, specific gravity, etc. etc. Quartz, galena, iron and copper pyrites, and many other minerals may be determined in this way. Further, by experience a shrewd estimation can generally be made of the percentage present of substances such as iron pyrites, and the experienced assayer need not conduct preliminary trials as to the oxidising or reducing nature of ores. He will judge quantitatively by inspection the approximate percentage of the various minerals present and flux his ores accordingly. The student, however, is recommended at the outset to rather distrust his mineralogical knowledge and make absolutely sure of such points.

(2) **Dry Tests.**—As the result of inspection the student may still be in doubt as to the composition of certain minerals present, and it frequently happens that the application of a few dry (blowpipe) tests will quickly and finally decide the doubtful point. The details of these tests have been given and need not be repeated, though here the student will require considerable skill in manipulation and in drawing conclusions from his tests, owing to the probable presence in many cases of conflicting substances. If such difficulties arise the student is referred to Moses and Parsons, Eudlich, Cornwall, or other authorities on blowpipe work.

By the aid of such tests combined with inspection the student should in many cases be able to determine definitely the presence or otherwise of elements such as sulphur, arsenic, antimony, copper, lead, iron, etc. etc.

(3) **Wet Tests.** — These in this case need only be applied when the previous tests fail or only give partial satisfaction. In the case of certain alloys and complex ores the student's skill in dry reactions may fail him;

in such cases he must depend on wet methods, his knowledge of which should now be sufficient to solve any problem of ordinary difficulty coming within the scope of the assayer's work.

The student, then, on receiving an ore for assay, having labelled it, should if possible obtain at least some of it in lump form. If this be impossible he should carefully examine the powdered ore with a strong lens. If there be sufficient ore it will be instructive to 'pan off' a few pounds weight and examine the concentrates (see Mechanical Assays). The magnet may be applied to the powdered ore to detect any magnetic particles. Having noted any conclusions drawn from inspection, he will next proceed to dry tests, and then to wet if necessary.

In certain cases a modification of the usual methods of qualitative separations may be adopted, with the result that sufficient accuracy is attained with a considerable saving of time, a point of much importance to the assayer. The following table will be found convenient if the student wish to ascertain, for example, the impurities in a lead button or a sample of base bullion.

TABLE FOR ALLOYS AND BASE BULLION.

Suspected to contain (besides *lead*) **antimony, tin, arsenic, copper, zinc,** etc.

Method.—Place in a 100 c.c. conical beaker or flask about 5 gm. fine powder (if brittle) or fine shavings (if malleable) of the base bullion. Carefully add 10 c.c. of strong HNO_3 and 5 c.c. of strong H_2SO_4. Gradually heat to boiling. Dilute, filter, and wash.

<table>
<tr><td colspan="2">Residue.
Contains Pb, Sn, Sb.
Boil with $H_2C_4H_4O_6$.
Filter and wash.</td><td colspan="3">Filtrate.
Contains Pb, As, Cu, Fe, Zn.
Pass H_2S and filter.</td></tr>
<tr><td>Residue.</td><td>Filtrate.</td><td>Precipitate.</td><td colspan="2">Filtrate.</td></tr>
<tr><td>Contains Pb, Sn. Dry and fuse with KCN. Cupel button obtained. Any Sn remains as a residue on the cupel.</td><td>Contains Sb. Pass H_2S. An orange-coloured pp. indicates Sb.</td><td>Contains As and Cu, etc. Dry and test by blowpipe reactions for As and Cu.</td><td colspan="2">Contains Fe, Zn, etc.
Boil off excess H_2S, add excess NaHO.
Boil and filter.</td></tr>
<tr><td></td><td></td><td></td><td>Precipitate.</td><td>Filtrate.</td></tr>
<tr><td></td><td></td><td></td><td>Test for Fe if necessary.</td><td>Add excess $HC_2H_3O_2$. Pass H_2S and a white pp. indicates Zn.</td></tr>
</table>

The scheme given is simply a modification of the methods previously employed in the qualitative analysis of alloys, and may be varied by the intelligent student as circumstances demand. The student will frequently find in practice that he cannot rigidly adhere to the schemes of text-books in every particular case; and in modifying such schemes to suit technical requirements, where accuracy and speed are necessary, it is absolutely essential that he should have a thorough grounding in theoretical and practical chemistry. Without this he

can never be more than a mere 'rule of thumb' assayer or analyst. It is essential that the student be acquainted with the accuracy of a reaction, and the effect of the presence of interfering elements on the reaction. Knowing these, he can proceed with some confidence to devise methods for particular cases. In quantitative analysis he should continually endeavour to ascertain the degree of accuracy of the methods employed. Certain methods of great accuracy he will find require a great expenditure of time ; and in technical analysis, where results are required quickly, accuracy may to some extent be sacrificed in favour of speed. Where this is done, the degree of accuracy or value of the results must be carefully ascertained, and in such researches a thorough knowledge of qualitative analysis is the best possible basis from which an attack may be made on these and other problems in assaying and metallurgical analysis.

CHAPTER VI.

INTRODUCTORY EXPERIMENTAL WORK.

THE EFFECT OF VARYING FURNACE TEMPERATURES.

(*a*) The Wind or Melting Furnace.

Principle.—According to the equation $2PbO + C = Pb_2 + CO_2$, 446 grains of litharge fused with excess of charcoal should yield 414 grains of metallic lead. If the temperature be too high, PbO volatilises, and this loss, which varies with the temperature and air present, can be checked by weighing the button from a given quantity of litharge.

Apparatus.—Wind furnace, tongs, moulds, crucibles (C) and lids, pulp scales, weights, etc.

Reagents.—Litharge and finely ground charcoal.

Details of Operation.—Prepare a low red fire in the furnace. Adjust the pulp scales. Take 6 pieces of glazed paper, each about 25 c.m. × 30 c.m., and number them 1 to 6. Weigh out 6 charges, each consisting of 10 gm. (or 100 grains) powdered litharge. Place one charge on each of the 6 pieces of paper.

Weigh out 6 charges, each consisting of ·5 gm. (8 grains) of finely powdered charcoal, placing one on each of the 6 pieces of paper. Carefully and thoroughly mix each of the 6 combined charges. This may be done either by transfer to a wedgwood mortar or by means of a spatula on the paper. The furnace will by this time require attention, and should be restoked to obtain a dull red heat.

Transfer charges 1 and 2 each to a crucible (Battersea round). On top of each charge, after transference to the crucible, add a cover of 2 gms. (20 grains) charcoal. Place the two crucibles in the furnace, sinking them till the coke is level with their top edges. This may be done either by building the coke up round the crucibles if the fire be low, or by making a cavity by aid of the tongs and inserting the crucible in the cavity; or, better still, two old crucibles (dummies) are built into the coke at the outset, and on removing them the crucibles containing the assays can be introduced into the cavities thus obtained. Place a lid on each crucible. Close the furnace door. Examine every few minutes till the crucibles become dull red, then allow them to remain in the furnace at this temperature for twenty minutes.

Meanwhile, clean two moulds, heat them till uncomfortable to the touch, oil or rub with graphite their interior surfaces. Remove each crucible in turn, and carefully pour into its respective mould. When cool (after five minutes or so), carefully remove the lead from each mould and weigh, taking care to collect any small prills of metal. Enter the results, with notes of the quantities of litharge, charcoal, time and heat of fusion, in your laboratory note-book.

Calculation of Results.—As 446 grams pure litharge should yield 414 grams lead, 10 gms. litharge should yield $\frac{10 \times 446}{414}$ gms. lead = 9·28 gms. lead. The student will probably obtain buttons weighing about 8 gms., the remainder being lost in fusion. The results, though inaccurate, will be compared with those from the remaining tests. The student must remember that the litharge is rarely pure. Now transfer charges 3 and 4 to crucibles, and insert the charged crucibles in the furnace in the cavities left by 1 and 2. Urge the fire, and when the temperature becomes bright red, allow the assays to remain at that temperature for twenty minutes. Remove, pour, and collect the lead as before. Enter the results in your note-book.

Now proceed with charges 5 and 6, urging the fire to its utmost to produce a white heat. Allow the charged crucibles to remain at this temperature for 20 minutes. Remove, pour, and note the results as before.

The student will find some difficulty at first in regulating the temperature. If he has carefully followed the instructions given, he should obtain three pairs of buttons. The buttons of each pair should not differ more than a few grains from each other. The weights of each successive pair of buttons should diminish as the heat increases after a red heat has been obtained. (Probably the middle pair will give the highest results.)

In reducing lead from litharge by means of charcoal *a certain temperature* is required before the reaction will take place. Any considerable increase above this temperature can only lead to loss by volatilisation of the litharge. Also, at this 'certain temperature,' *a certain time* is required to reduce all the lead from a given quantity of litharge. The temperature being constant, the time depends largely on the intimacy of mixture of the charcoal and litharge; this, again, depends on the degree of fineness to which the two substances are ground. As a general rule, the finer the grinding and mixture the better the results. When once this necessary period of heating has elapsed, any further heating can only lead to loss, the lead being liable to reoxidation, though with the excess of charcoal present this loss must be slight.

So far the student has kept the time constant, and has varied the temperature. Time will now be considered.

The Effect of Variations in Time.

Weigh out 6 charges as before.

Place 1 and 2 in the furnace and keep at a bright red heat for *five minutes*. Remove, pour, collect and weigh buttons. Note results.

Place 3 and 4 in the furnace at the same temperature, but for *twenty minutes*. Treat as before, noting results.

Place 5 and 6 in the furnace at the same temperature, but for *sixty minutes*. Again note results.

These results will give the student some idea of the influence of time on an assay. Besides the losses mentioned, others, such as the formation of silicate of lead, occur. This loss may to some extent be avoided by coating the interior of the crucible with graphite. When considering the fire-assay of lead ores the student will see that certain precautions are taken to prevent the formation of silicates of lead. He will see that to obtain the least possible results other charges than that just given are adopted. The experiments just described are given not for the purpose of estimating the lead in litharge, but to show the student the effects of varying temperature and time on an assay.

(*b*) The Muffle Furnace.

The Effects of varying the Temperature.

Principle.—If a weighed quantity of silver be wrapped in sheet lead and cupelled in a muffle furnace, and the resulting button be weighed, any difference in weight (neglecting for the present the small quantity of silver in the lead) represents loss in cupellation. This loss varies with different temperatures.

Apparatus.—Muffle furnace and tools, cupels, balance sensitive to $\frac{1}{1000}$ grain, weights, etc.

Reagents, etc.—Sheet lead, test silver.

Details of Operation.—Weigh out three charges as follows, the lead being weighed on the pulp scales, and the silver on the finer balance,

Silver,	. .	0·2 gm. (or 3 grains).
Lead,	. .	10 ,, (or 150 grains).

The student will meet with some difficulty in obtaining the exact weight of silver. To save time he may place on the pan approximately ·2 gms. and note the exact weight, perhaps ·242 gm. or ·175 gm.

Wrap each lot of silver in the sheet lead. Place three good dry cupels in the furnace, which should be at a *red* heat. After a few minutes insert charge 1 in its cupel. Close the door till cupellation commences. Open the door and regulate the temperature, so that feathery crystals of litharge form round the inner rim of the cupel. When finished, carefully remove the cupel, taking precautions to prevent the bead 'spitting.'

When cool remove the bead, and free it from bone ash by gentle tapping with a hammer. Weigh the bead and note the result.

Urge the fire, and when the muffle is at a *bright red* insert charge 2 in its cupel. Continue the cupellation at a bright red, and when finished remove as usual; cool, clean, and weigh. Note the results.

Urge the muffle still further, till almost a *white* heat is obtained. Insert charge 3. Maintain as nearly as possible a white heat during cupellation. Remove, cool, and weigh as before. Note the result.

For comparison, the student may tabulate the results of these three experiments as follows :—

Silver taken.	Weight Bead.	Temperature.	Loss.
(1) ·204 gm.	·202 gm.	Red.	·002 gm.
(2) ·198 gm.	·195 gm.	Bright Red.	·003 gm.
(3) ·212 gm.	·205 gm.	White.	·007 gm.

The figures quoted, though imaginary, indicate to the student the probable results of his experiments, and demonstrate the increase in the loss of silver with increasing temperature.

The student is referred to more advanced text-books for details of experiments regarding other losses, such as absorption of gold and silver by the cupel, etc. Want of time will prevent the student at this stage from following up these researches, and in the following pages brief notes will be given, where necessary, regarding the effect of such losses on the accuracy of an assay, and on the means of reducing such losses to a minimum.

The purpose of the present experiment will be served if the student determine for himself the important part played by temperature in cupellation. From the nature of the case experiments regarding time are not so applicable here as when dealing with the wind furnace.

(*c*) The Influence of Temperature and Time on the Roasting of Sulphide Ores.

Principles of Experiment.—Samples of the 'roast' are taken at various stages of the operation, and the state of the desulphurisation and other points of value determined approximately by suitable tests.

Apparatus.—A furnace (preferably muffle), roasting dishes (8 cm.), the usual furnace tools and chemical apparatus for qualitative work.

Reagents, etc.—A sulphide ore containing copper, iron, and sulphur, also the ordinary qualitative chemical reagents.

Details of Experiment.—Raise the temperature of the muffle to a very dull red. Place in the roasting dish about 20 gms. of the ore which has been ground and passed through a 60 sieve. Transfer the dish and charge to the muffle.

(1) When a pale blue flame appears on the surface of the charge remove about 5 gm. (one quarter of the ore). On removal, smell the partially roasted ore and note the smell of burning sulphur (SO_2). Shake up these 5 gm. with about 100 c.c. H_2O in a small flask. Repeat the shaking several times. Filter, and to a portion of the filtrate add NH_4HO in excess. Little or no **Cu** or **Fe** will be detected in this filtrate, indicating that, so far, soluble compounds of these elements have not been formed to any extent.

(2) After the removal of sample (1) carefully stir (with a long wire bent at one end) the charge in the furnace. Continue stirring, raising the temperature till the blue flame ceases. Remove a sample as before and treat with water, filtering and adding ammonia as before. The presence of **Cu** and **Fe** should be very marked at this stage.

(3) Raise the temperature and continue the roast; after the lapse of 30 minutes remove a small sample and test again for soluble sulphates. Continue the roast, raising the temperature till no reaction is obtained for soluble sulphates. This last stage takes a considerable time. The student may now test by the usual methods the thoroughly roasted ore and ascertain whether traces of sulphur still remain. Unless subjected to repeated roastings at a high temperature with the aid of oxidisers it will always be found that a small amount of sulphur is left in an ore after roasting. When roasting gold ores previous to crucible assay, careless or hasty work on the part of the student will result in the presence of a considerable percentage of sulphur, which in the crucible acts as a reducer. Larger buttons than usual are obtained, the sulphur assisting the charcoal or other reducer used.

If time permit, the student may further experiment on ores containing zinc, arsenic, etc. For the present, however, the average student, whose time is limited, had better strictly confine his attention to the work laid down in these pages.

Estimation of the Reducing Power of Charcoal, Flour, and Argol.

Method of Experiment.—The reducing powers are compared by ascertaining the amount of lead which one part by weight of each of these reducers can extract from litharge when subjected to the action of heat in a crucible.

Apparatus required.—As in experiments on the wind furnace.

Reagents. — Finely powdered litharge, charcoal, flour, argol, glass powder, and soda.

Details of Experiment.—

(1) Weigh out two charges of the following—

Litharge	1	A.T.	or	30	gms.	or	400	grains
Soda	$\frac{1}{2}$	,,	,,	15	,,	,,	200	,,
Glass Powder	$\frac{1}{2}$	,,	,,	15	,,	,,	200	,,
Charcoal	$\frac{1}{40}$	,,	,,	0·75	,,	,,	10	,,

The weights are here given in three systems, but in future only one system will be given, from which, if necessary, the student may obtain corresponding values in other systems by simple calculations. Mix intimately the two charges. Transfer to F crucibles, cover, fuse in a bright red fire till the surface of the charge appears tranquil, *i.e.*, until all frothing has ceased, and the surface of the molten charge is slowly moving in gentle waves. Pour into clean, hot, oiled moulds (preferably conical). Care must be taken in pouring that no lead sticks to the sides of the crucible. The cause of this is generally uneven heating, the top of the crucible projecting above the surface of the coke. The remedy is proper firing.

When cool, remove from the moulds; break away and clean the two buttons, weigh them, and note their weights, which should not differ more than 5 grains.

(2) Weigh out two charges of the following—

Litharge . .	30 gms.
Soda . . .	15 ,,
Glass Powder .	15 ,,
Flour . . .	2 ,,

Mix, fuse, pour, clean buttons, and weigh as before. Note the results.

(3) Weigh out two charges of the following—

Litharge . .	30 gms.
Soda . . .	15 ,,
Glass Powder .	15 ,,
Argol . . .	4 ,,

Treat as before, and note results.

Calculation of Reducing Power.—Three sets of results are obtained, *e.g.*—

(1)	(2)	(3)
21·2 gms. 21·5 ,, Mean 21·35 ,, Now ·75 gm. *Charcoal* gives 21·35 gms. Lead; therefore 1 gm. Charcoal gives 28·5 gms. Lead.	23·4 gms. 23·6 ,, Mean 23·5 ,, Now 2 gms. *Flour* give 23·5 gms. Lead; therefore 1 gm. Flour gives 11·7 gms. Lead.	24·0 gms. 24·3 ,, Mean 24·15 ,, Now 4 gms. *Argol* give 24·15 gms. Lead; therefore 1 gm. Argol gives 6·0 gms. Lead.
Reducing Power Charcoal, 28·5.	**Reducing Power Flour, 11·7.**	**Reducing Power Argol, 6·0.**

Accuracy of Results.—Considerable practice is necessary in order to obtain much accuracy, but the results obtained in these experiments will be sufficient for the student's purpose. The results will vary with the quality of the reducer

taken. Argol, for example, varies from 5 to nearly 7. In his future work the student will be instructed in certain cases to add sufficient reducer to obtain a button of 20 gms. Supposing the figures quoted represent the student's results, then either $\frac{20}{28{\cdot}5}$ gms. charcoal, or $\frac{20}{11{\cdot}7}$ gms. flour, or $\frac{20}{6}$ gms. argol may be used. In all such calculations decimals may be disregarded, and the nearest unit adopted as a divisor.

Estimation of Silver in Litharge, Sheet and Granulated Lead.

Method adopted.—Weighed quantities of sheet or granulated lead are cupelled under certain conditions, and the silver bead obtained is weighed. In the case of litharge, the lead is reduced and then cupelled.

Apparatus.—Wind and muffle furnaces, balance, etc., as before.

Reagents.—As before, with the addition of borax and salt.

Details of Estimation.—In carrying out the following operations, the student must carefully note the conditions under which he is working, as the results here obtained will be made use of in subsequent assays, in which similar conditions must be observed. These remarks apply particularly to cupellation.

Weigh out two charges of the following—

Litharge, . .	60 gms.
Soda, . . .	30 „
Glass Powder, .	20 „
Argol, . . .	3 „

Mix, fuse, pour as usual. Hammer the resulting button into a rough cube. Transfer to a cupel, and carefully cupel at a low temperature producing 'feathers.' Remove the cupel as soon as finished, and weigh the silver bead. This amount of silver must always, therefore, be deducted when 60 gms. litharge are used in a silver assay. Proportionate deductions are made with other quantities of litharge. In order that this deduction be accurate, all buttons should be cupelled as nearly as possible at the same temperature.

In the case of sheet or granulated lead, transfer the 60 gms. charge, without fluxes, to a $2\frac{1}{2}''$ scorifier, and when the eye has closed in, pour, and then cupel the button. Weigh the bead, and the necessary deduction is obtained as before.

The Effect of Impurities on Cupellation.

Method of Experiment.—Weighed quantities of other metals will be added to weighed quantities of silver and lead, and after cupellation the coloration of the cupel and the appearance of the bead indicate to a certain extent the impurity present.

Apparatus.—The muffle furnace, balance, and accessories.

Reagents, etc.—Gold, silver, lead, copper, tin, antimony.

Details of Experiment.—Weigh out five charges approximately as follows :—

(1)	(2)	(3)	(4)	(5)
Ag 0·1 gm.	Ag 0·1 gm. Au 0·2 „	Ag 0·1 gm. Cu 0·2 „	Ag 0·1 gm. Sb 0·1 „	Ag 0·1 gm. Sn 0·1 „

Wrap each of these five charges in 5 gm. sheet lead, and cupel at a *bright red* heat. Tabulate results as follows:—

No.	Weight Bead.	Appearance of Bead.	Appearance of Cupel.
1 2 3 4 5	Results to be entered by the student.		

In his subsequent work the student will gain further experience in the effects of these and other impurities on cupellation, and also as to the effects of varying quantities of one and the same impurity.

The Effects of Impurities on Scorification.

Method of Experiment.—A number of charges of a quartzose ore are prepared, and weighed quantities of certain substances are added to the various charges. The effects on the charge and dish are noted.

Apparatus.—The muffle furnace, pulp scales, and accessories.

Reagents.—Quartz, grain lead, borax glass, copper, iron, cobalt, and manganese. In place of cobalt and manganese the oxides of these metals may be used.

Details of Experiment.—Weigh out five charges as follows—

(1)	(2)	(3)	(4)	(5)
5 gms. Quartz. 40 ,, Lead.	5 gms. Quartz. 40 ,, Lead. 2 ,, Iron.	5 gms. Quartz. 40 ,, Lead. 2 ,, Copper.	5 gms. Quartz. 40 ,, Lead. 2 ,, Cobalt (Oxide).	5 gms. Quartz. 40 ,, Lead. 2 ,, Manganese (Oxide).

Carefully mix each of the five charges, and scorify at a *bright red* heat, assisting the operation with a pinch of borax glass and a higher temperature where necessary.

Tabulate the results as follows:—

No.	Appearance of Scorifier.	Appearance of Slag.
1 2 3 4 5	Results to be entered by the student.	

CHAPTER VII.

THE ASSAY OF TIN ORES

THE student is required to determine the percentage of metallic tin by fire-assay in

(*a*) **Clean Stream Tin.**
(*b*) **Poor Ore containing Wolfram and other impurities.**

(*a*) **Clean Stream Tin, SnO_2.**

Principle of Assay.—The student will find, on consulting advanced text-books, that various methods of assay are recommended; methods varying in quantities of ore and fluxes, and, to an unaccountable degree, in temperature and time of fusion. Here only one method will be given, and the student must practise this method till accurate results are obtained; then, if time permits, he may experiment with other methods. As in photography the amateur who changes about from one developer to another seldom does good work, so here the student who attempts all methods seldom masters any.

The method here described depends on the reaction expressed in the following equation—

$$SnO_2 + 2KCN = Sn + 2KCNO$$

Apparatus.—The wind furnace, pulp scales, and minor accessories.

Reagents.—The sole reagent is potassium cyanide, that sold as gold cyanide being most suitable.

Details of Operation.—The stream tin is sampled and reduced as usual, the final assay sample being passed through an 80 sieve.

The following charge is weighed out in duplicate—

Ore,	10 gms.
Cyanide,	30 „

In the bottom of each crucible (E) ram about 5 gms. **KCN**, then add the above charge, and finally add about 5 gms. **KCN** as a cover.

Transfer the crucibles, and carefully bed them in a *bright red* (not a white) fire. Fuse for twenty-five minutes. Remove the crucible, and if the edges are still bright red pour the charge; if not, allow it to remain in the crucible till cold. Break the crucible and remove the button. Generally, the student will find that by quick and careful pouring good results may be obtained. The slag may be (and should be) examined by grinding and panning (see "Panning"), and any prills obtained are added to the result.

Note the weights of buttons obtained. The student must continue his practice till uniform results are obtained, and to do this he must have the furnace well under control.

Calculation of Results.—As the result is generally required in percentage of tin, the weight of button in grams is multiplied by 10, *e.g.* a

sample of stream tin gives buttons averaging 7·32 gms.; the percentage of tin is therefore 73·2.

Accuracy of Results.—Care and much practice are necessary in firing tin ores. Under good conditions, that is, with a clean ore and proper firing, the error is not greater than 0·5 per cent., *e.g.* if an ore by fire-assay yielded by the Cyanide method 72·3% tin, the true tin contents are not more than 72·8%, nor less than 71·8%.

(*b*) Poor Ore containing Wolfram and other impurities.

Method of Treatment.—As arsenic and sulphur may be present besides wolfram and decomposed granite or other rock, it is evident that if the oxide of tin in a fairly clean state is required, some method of purification must be adopted. As and S will be eliminated by roasting, the light gangue by panning, and any oxide of iron and tungsten by treatment with suitable chemicals.

The remaining oxide of tin is then treated as before.

Apparatus.—Furnace for melting and roasting. A prospector's 'gold' dish or other 'panning' or 'vanning' appliance. Chemical apparatus, pulp scales, etc.

Reagents.—Potassium cyanide, ammonium carbonate, hydrochloric acid, ammonia (20E. NH_4HO), rain (or distilled) water.

Details of Operation.—The ore is crushed and sampled till one pound or 400 gms. is obtained. This sample is passed through a 60 sieve. If S and As be present, add a little ammonium carbonate, and roast the sample in a sheet-iron vessel on top of the wind furnace, the temperature having been raised to a bright red. During roasting add a little more ammonium carbonate. When the S and As have been removed, transfer the charge to the gold pan, under which is placed a larger basin to catch the 'tailings.' Run into the gold pan about a quart of water, and with one hand work the charge about till thoroughly moistened (takes two or three minutes), allow the sediment to settle for a minute, and carefully pour off the liquid into the basin below. This second basin is set over a sink to conveniently dispose of subsequent overflow.

'Panning' or 'vanning' proper now begins. The lip of the gold pan is dipped in the second basin till enough water is lapped up to cover the ore about half an inch. The ore and water are then agitated by a peculiar circular and jerking motion (best learned by practice), with the object of settling the heavier particles of tin ore and keeping the light gangue partially suspended. Some operators allow a continual discharge to proceed by inclining the pan; others work the ore down to the angle of the pan, or between the angle and the ripple near the lip, and then wash away the top layer (about $\frac{1}{10}$ the total depth). This operation is continued till the dark coloured oxide of tin begins to show through the lighter gangue. The remaining grains of sand are removed as far as possible by further panning. The student should now take the tailings in the second basin and again pan them in the gold dish. He will generally find that in the first operation he has allowed some oxide of tin to escape, and even on the third repetition he may still find that he is losing tin. (For practice in panning the student is recommended to take three small specks of gold, place them in a few pounds of earth, and pan off the mixture till he separates the three specks.)

From an ore containing approximately 2% tin a residue of about 14 to 20 grams will be left as the result of the concentration.

This residue is now transferred to a beaker or porcelain basin with cover,

and gently boiled with strong HCl to dissolve iron salts and wolfram. Half an hour's boiling generally suffices. If wolfram be present, a yellow residue of tungstic acid (WO_3) forms. The HCl is removed by decantation, and then the tungstic acid is removed by solution in excess of strong NH_4HO, a soluble tungstate being formed and removed by decantation. The residue is now dried, weighed, and fluxed with the same proportion of cyanide as before.

Calculation of Results.—The percentage of tin is found thus:—If 400 grams of ore give, for example, 8 grams of metallic tin, then 100 grams give 2 grams of tin; that is, the ore contains 2% of tin.

Accuracy of Results.—The main source of loss in this assay lies in the operation of concentration. The only remedy is continual practice and repeated treatment of the tailings, and even then ores may be met with which even experienced vanners find difficult to treat. The purification process by acid and ammonia is very desirable where a clean button of tin is desired. The button, when pure and formed in a mould of fair depth, should be silvery white in appearance, and have a dimple on the top. If these conditions are not present, the student should hammer out the button and subject a portion of it to qualitative analysis, the result of which will give him a clue to the impurity; and his method of treatment must be varied accordingly.

It is difficult to estimate the degree of accuracy of the results of this assay, but with careful concentration and purification of the concentrates, and proper firing, the error should not be greater than two points in the first decimal place; thus, an ore containing 1·8% tin should yield results not lower than 1·6%.

CHAPTER VIII.

THE ASSAY OF LEAD ORES.

The student is required to determine by fire-assay the percentage of lead in—

(*a*) **The sulphide, Galena** (PbS).
(*b*) **An oxidised ore** containing **Cerussite** ($PbCO_3$), **Anglesite** ($PbSO_4$), etc.

(*a*) The sulphide, Galena

Methods employed.—Regarding the methods employed authorities vary widely; here two methods are given for sulphide ores,—the *Soda and Argol* (or *Nail*) *method*, and the *Cyanide method.*

The reactions are expressed as follows—

$$7PbS + 8NaHCO_3 = 4Pb + 3(Na_2S,PbS) + Na_2SO_4 + 4H_2O + 8CO_2$$

$$Na_2S,PbS + Fe = Pb + Na_2S + FeS$$

$$PbS + KCN = KCNS + Pb.$$

First Method (Soda, Argol and Nails).

Apparatus.—The wind furnace, pulp scales, crucibles, etc.

Reagents.—Soda, carbonate of potash, argol, salt, nails or wire.

Details of Operation.—The ore (clean galena) is reduced, sampled, and an assay sample obtained which has passed through an 80 sieve.

Weigh out in duplicate the following charge—

Ore, ...	10 gms.
Soda, ...	15 „
Carbonate of Potash, . . .	5 „
Argol, ...	5 „

Thoroughly mix the charges on glazed paper, and transfer them to their crucibles (F). In each crucible insert two loops of fencing wire, tied together at their bends with iron wire, and of such a length that they come to about a quarter of an inch from the top of the crucible. When the loops are inserted add a cover of 5 to 10 gms. salt. Carefully bed the crucibles in a good coke fire, and build the coke well above the top edges of the crucibles. Place covers on the crucibles and a few lumps of coke on the covers.

Keep the fire between dull red and bright red (that is, a red), and never let it rise above a bright red. The time of fusion varies with the fire and ore, but at the end of ten minutes the cover may be removed and the charge inspected now and then, replacing the cover and coke after inspection. When frothing ceases, allow the charge to remain in the furnace for five minutes. Then pour into a hot, greased conical mould, after withdrawing

the wire loops, any adhering prills of lead being removed by washing the wires in the slag. If the top edges of the crucible have cooled below a red heat the charge should not be poured. The button is in this case removed by breaking the crucible when cold.

Detach the slag; hammer the button into a cube and weigh it. Note the result and all details of firing, etc.

Calculation of Results.—The percentage is obtained by multiplying the weight of the button in grams by ten.

Accuracy of Results.—A difference of opinion exists as to the merits of this and of the Cyanide methods. Neither is as accurate as the gravimetric estimation. With a fairly clean Galena both methods give results with an error + or − of one unit, *e.g.* if the gravimetric process gives 75% of lead, these processes will give from 74% to 76%. On the whole, the evidence is slightly in favour of the Cyanide method, but before proceeding further the student must continue his practice till his results are uniform and satisfactory. Even if he has to run through thirty or more assays, the time so employed is amply repaid by the confidence gained.

The following tabulation indicates the causes of inaccuracy:—

Cause.	Remedy.
(1) Galena sublimes before decomposition.	Avoid a high temperature.
(2) Lead oxidises.	Careful covering of charge, and quick removal when finished.
(3) The lead button may contain antimony, copper, bismuth, iron, etc.	Wet method must be used.
(4) Arsenic removes lead into the slag.	,,

Briefly, the fire-assay of lead is unreliable when other reducible metals are present, and when these are absent it is accurate to about one unit on rich ores.

Second method (Cyanide).

Apparatus.—As before.

Reagents.—Potassium cyanide salt.

Details.—Weigh out in duplicate the following:—

Ore, . .	10 gms.
Cyanide, .	30 ,,
Salt cover, .	about 5 gms.

Mix charge, cover and insert in the furnace as usual. Fuse for 15 minutes between a red and a bright red, firing as before. Pour and weigh the buttons.

Calculations.—As before.

Accuracy of Results.—Here again practice and care are necessary. With a clean rich galena good results are obtained, but when impurities such as copper, antimony, bismuth, etc. are present the results are worthless. To

prove this statement, let the student add to one of his charges either antimony or copper, and then examine the resultant button. From this the student will gather that before assaying a strange lead ore, he must examine it qualitatively for these or similar substances. If these be present to any extent, fire methods must be replaced by wet processes.

(*b*) Oxidised Ores containing Carbonates and Sulphates of Lead.

Method.—For carbonates the following charge serves:—

Ore,	10 gms.	Salt cover
Soda,	15 „	
Potassium carbonate,	5 „	
Argol,	5 „	

But where sulphates are present the Cyanide method is preferable; in fact, for both classes of ore, when fairly pure, this latter method is both simple and accurate.

Details of the operations need not be repeated. Let the student weigh out four charges,—two of the charge just given, and two of the cyanide charge as previously given. Fire carefully, and compare the results.

In conclusion, the student is reminded that *practice* and careful *observation* are necessary before success can be obtained. Where unsatisfactory results are obtained, the student should see that—(1) The ore is ground sufficiently fine; (2) That the fluxes are *well* mixed with the ore, intimate mixture being necessary; (3) That with *every* assay he note the state of the fire, the time that elapses before the charge fuses, the time of 'frothy' fusion, the time of tranquil fusion; (4) That he examine qualitatively the lead button and determine what foreign ingredients are present; (5) If results are low, examine the slags for lead.

By these and other tests the source of error may be located, and from the nature of the error the student will see whether his work is at fault, or, as may be the case, that the Fire method is unsuitable to the ore in question. It is only by taking pains that the student can arrive at any certainty as to the value of his work, and without certainty an assay is of little value. The student has not the time necessary to fully check all his operations, but wherever reasonably practicable he should make some attempt in this direction, and also should consult reference works on such points.

CHAPTER IX.

THE ASSAY OF GOLD IN ITS ORES AND PRODUCTS.

THE student is required to estimate gold in—

I. **Ores:**
- (*a*) **Clean (Siliceous) Ores.**
- (*b*) **Basic Oxidised Ores.**
- (*c*) **Sulphide Ores.**
  - (1) Iron Pyrites.
  - (2) Cupriferous.
  - (3) Antimonial.
  - (4) Arsenical.
- (*d*) **Telluride Ores.**

II. **Products:**
- (*a*) **Mattes.**
- (*b*) **Blister Copper.**
- (*c*) **Gold Bullion.**

Introductory.—In order that the subsequent descriptions of methods may not be unduly lengthened by explanations regarding fluxing and other details, some general principles and notes have been collected, and are here laid down for the guidance of the student, who before going further should again read the chapter (II.) on Reagents and Fluxes.

The two most important fluxes used in the assay of gold ores are *borax* and *soda*; borax being used as a flux for CaO, FeO, and other like bases; soda for SiO_2 and silicates; $1\frac{1}{3}$ Na_2CO_3 or $2\frac{2}{3}$ $NaHCO_3$, fluxing 1 SiO_2 by weight. The compounds thus formed (borates and silicates) are fusible at a lower temperature than the metallic oxides, silica, or silicates alone.

Next in importance are the lead oxides *litharge* and *red lead*. Besides acting as collectors of precious metals, the monoxide is a powerful base, and in certain cases—for instance, when oxides of copper are present—it assists in the formation of readily fusible double silicates. Litharge is best suited for quartz ores and red lead for pyritic ores when an oxidising action is required.

Of the remaining fluxes *fluor spar* is of importance, being of service with ores containing considerable proportions of sulphates of barium and calcium or calcium phosphate. The action here seems to be partly that of a change of solvent, the fluidity of the charge being increased. Fluor spar also removes SiO_2 as SiH_4.

As a general rule, $2\frac{1}{2}$ to 3 parts by weight of flux to 1 part of ore give a fusible slag, and where this is not so the remedy lies in the nature and proportion of the fluxes used, not in the quantity. It should be noticed that too fusible a mixture may be obtained, with the result that the lead has not the opportunity of thoroughly collecting the precious metals, as the lead sinks too rapidly to the bottom of the crucible. With ores containing much FeO the addition of alkaline carbonates forms double silicates of

such a nature that the slag formed is very fluid if a large excess of carbonates is used; therefore, as the metallic oxides in an ore increase, diminish the proportion of soda and increase the proportion of borax, litharge, and charcoal (see following notes on Reducers), but for ores containing much lime alumina or zinc oxide, the proportion of alkaline carbonates can be considerably increased.

Regarding reducers, the student will find that *flour* or *argol*—preferably the latter—is preferable to charcoal, for the following reasons: The larger bulk of argol (4 times) permits of a much more intimate mixing of the reducer and charge, the whole charge, on fusion, thus becoming evenly permeated with very minute globules of metallic lead. Also in routine work less care need be exercised in weighing the argol. One grain error in weighing or measuring the reducer produces a difference of 24 grains lead with charcoal and only 6 grains with argol.

Besides reducing litharge or red lead to metallic lead, it is frequently necessary to reduce ferric oxide (Fe_2O_3) to ferrous oxide (FeO). With hematite ores or roasted pyritic ores, as the ferric oxide is infusible and renders the slag pasty, and as ferrous oxide readily forms fusible compounds, it is necessary to reduce the higher to the lower oxide. If charcoal be used for this purpose, about 1 grain of charcoal is required for every 10 grains of ferric oxide present.

Salt is used largely as a cover to protect the charge from oxidation, the layer of fused salt floating on the surface of the charge. Further, it is applied in 'pinches' to 'settle' a charge which is 'boiling' too violently, the action resembling that of oil on water.

The student is advised in every case to bring his chemical knowledge to bear, and to proportion his ore and fluxes rationally, and not by the so-called universal formulæ given in some text-books. The analogy between the blast furnace and charge and the crucible and charge is very close from the chemical standpoint, and the varied nature of the ores treated demands in both cases a thorough grasp of the underlying principles, and not a slavish following of some universal formula supposed to suit all classes of ore.

(*a*) **Clean (Siliceous) Ores.**—These ores contain *gold*, a little *silver*, over 95% *silica*, and a small quantity of metallic oxides.

Method No. 1—Crucible.

The *silica is fluxed* partly by soda and partly by litharge, forming double silicates. According to the equations

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$
$$PbO + SiO_2 = PbSiO_3$$

1 gm. Na_2CO_3 unites with ·57 gm. SiO_2 and 1 gm. PbO unites with ·27 gm. SiO_2. Generally, for every 1 gm. ore, about 1 gm. Na_2CO_3 is added; this leaves about ·43 gm. SiO_2 (1 − ·57) to be fluxed by PbO. This requires $\frac{43}{27}$ gms. = 1·6 gms. PbO. Further, a button of about 12 to 15 gms. lead is required, and this brings the total PbO up to about 2 gms. for every 1 gm. of ore. A little more soda and less litharge, or *vice versa*, may be used. A small quantity of borax is added to *flux the metallic oxides* present. Sufficient *reducer* is used to obtain a button of the required weight. Salt is added as a *cover*.

The lead button thus obtained is *cupelled*, the silver and gold being obtained as a bead.

The silver in the bead is dissolved (after *inquartation*) by nitric acid, leaving the gold, which is then weighed.

Apparatus.—Wind and muffle furnaces and tools, pulp scales, assay balance, weights, porcelain cups, cupels, crucibles, and the usual accessories.

Reagents.—Soda, litharge, argol, borax or borax glass, salt, test silver, parting acids, etc.

Details of the Assay.—Reduce and sample the ore, passing the final sample through an 80 sieve. (In this and all assays the student should make a point of attending to his furnace before weighing out his charge.)

Weigh out in duplicate the following charge—

Ore, . . .	30 gms.	
Soda, . . .	30 „	
Litharge, . .	60 „	} Salt cover 10 gms.
Borax Glass, .	10 „	
Argol, . . .	2½ „	

Note.—If the bicarbonate of sodium be used, a greater weight must be taken to flux the same amount of SiO_2 (Na_2CO_3 is equivalent to $2NaHCO_3$), 106 parts by weight of Na_2CO_3 being equal to 144 parts by weight of $NaHCO_3$.

Thoroughly mix the two charges; transfer them to their crucibles (G); place the salt covers on the charges and transfer the charged crucibles to a red fire. Cover with lids, placing the lid so that it projects a little over one side to allow the insertion of a poker to wedge up the lid if it happens to stick fast. If the charge after fusion shows signs of boiling over, add a little salt now and then till the violent effervescence ceases. Fuse at a red heat for 5 minutes, and at a bright red for 20 to 25 minutes. By this time the charge should be in a state of quiet fusion.

Remove the lids; withdraw and pour the charges into clean hot moulds, gently tapping each crucible on the furnace top before pouring, and at the same time giving a slight circular swirl to the crucible to wash the sides with the slag. When the mould has cooled sufficiently to solidify the lead, the slag and lead are removed and the slag broken off the button, which is then hammered into a cube with flattened corners. It is important that all the slag be removed by the hammering. The student will learn by experience that many assays are lost by undue haste in tipping the charge out of the mould before the lead cools, and that a cupellation may be spoiled by carelessness in cleaning the button.

The buttons obtained have now to be cupelled, but the student will find it advisable to repeat the work and obtain two more buttons before firing the muffle, which is to be heated between a red and a bright red.

Place four good cupels in the muffle, and in about five minutes remove them with the tongs and examine them for cracks, rejecting any showing faults. Replace the good cupels. Place the lead buttons carefully on the cupels, one on each. Close the doors and keep them so till the layer on top of the molten lead clears, that is, becomes bright and glowing. Now open the doors and continue the cupellation so that 'feathers' just form. Towards the end of the cupellation the alloy becomes nearly spherical in shape, and bright rainbow-coloured bands or rings rapidly move from the centre outwards, till finally they disappear, and a round bead remains and appears to rotate rapidly. The doors may now be closed or the cupel shifted to a hotter spot to remove the last traces of litharge.

As there is generally little silver in the ore that is now being assayed, the cupel may be removed at once and placed on a sheet-iron cupel tray. The time

of cupellation depends on the size of button and the temperature and quantity of air present, and on the average is from 30 to 45 minutes for a button of about 16 gms.

The four cupels and beads now rest in the cupel tray. Take four small porcelain crucibles about 2·5 c.m. in diameter, and taking each cupel in turn remove the bead carefully and steadily with a pair of suitable forceps and place it in a cup, and place the cup on the cupel. Remove the tray and contents to a small anvil with polished face. Examine each bead, and if any bone ash is attached fold the bead in a small slip of paper (to prevent it rolling away) and flatten with a few taps on the anvil and rub between the paper.

Weigh each bead on the assay balance, the weights giving the gold and silver present. The gold has now to be separated from the silver. The student will find in bullion assaying that great care is taken in proportioning the silver to the gold, in the proportion generally of $2\frac{1}{2}$ silver to 1 gold, but here it is sufficient for all practical purposes to add, if necessary, sufficient silver to obtain from 3 to 5 or 6 parts of silver to 1 part of gold. Therefore, if the bead appears silvery white, add about its own weight of silver, but if yellow, add about three times its own weight of silver. This added silver is roughly weighed out (with practice it is judged by sight by cutting given areas from a ribbon of silver of uniform thickness), preferably as foil, in which the bead is then wrapped and transferred to a small cavity in a piece of charcoal, and fused up for a minute or so with the mouth blowpipe. A hot pointed flame gives the best results. To secure an even alloy of the gold and silver the bead must be heated till it appears as a white spinning globule. (Large beads must be cupelled.)

Each bead is thus treated and replaced in its cup. The beads are then, each in its turn, flattened on the anvil till about the thickness of an ordinary visiting card, and then replaced in their respective cups.

Fill each cup about two-thirds full of parting acid No. 1. Place the four cups in order on a hot iron plate or sand bath and heat till the solvent action appears to cease—generally three to five minutes—then remove the cups and decant the liquid down a glass rod into a 'waste silver' bottle. No. 2 acid is now used in the same manner for about three to five minutes' heating, but avoiding boiling. (As before mentioned, the use of only one acid much facilitates the operation and gives accurate results.)

Remove the cups, decant and wash twice by filling up with distilled water from the wash bottle. By a little care and dexterity the washing and decantation can be carried out quickly and accurately, the black gold residue being retained in the cup.

At the last decantation drain the cup well, and turn it so that the last drop of water lies away from the gold. In this position dry it on the plate or sand bath. When dry, remove with the forceps and direct a strong O.F. by the mouth blowpipe on the outside of the crucible nearest to where the gold lies. In ten or twenty seconds the black residue becomes yellow. Now place the cup back on its cupel to cool, and treat the other beads in the same manner, returning each cup and bead to its respective cupel. When cool, take the tray into the balance room and weigh the gold obtained. This is done by removing the little pan to the front of the balance case and then bringing up the cup to the pan and carefully brushing in the gold with a fine brush on to the pan, which is then replaced and the gold weighed as usual. The student must see that his cups are clean, and that he transfers no bone ash from the cupels to the balance, also that he checks the balance frequently when weighing a number of beads, also that his 'rider' agrees with his weights.

Calculation of Results.—The student's note-book shows, say, the following:—

Ore taken, 30 gms.
Gold + silver, 0·0042 gm.
Gold, 0·0035 gm.

By subtraction,

Silver, 0·0007 gm.

But by previous assay the litharge was found to contain say 0·0009 gm. silver per 100 gms. litharge, therefore 60 gms. litharge yield 0·00054 gm. silver. That is

30 gms. ore contain 0·0035 gm. gold
0·00016 „ silver

By proportion, the gold and silver per ton may be calculated, or from a gram table, thus:—

Refer to the 40 gms. table.

	oz.	dwt.	gr.	
·0005 =	0	8	2·5	per ton.
·0030 =	2	8	15	„
	2	16	17·5	„
30 gms., then, give	3	15	15	gold per ton.

The silver may be calculated in a similar way.

If a number of assays with 30 gms. charges of ore have to be done, a 30 gms. table should be constructed on the principles previously laid down.

If the value of pure gold be £4, 4s. 11d. per oz., the value of the gold in the ore may be calculated. Similarly, assuming the value of silver to be 2s. 3d. per ounce, the value of the silver contents is ascertained. Here again, however, tables should be constructed. A 'gold' table from 1 grain to 1 ounce on the basis of £4, 4s. 11d. per ounce, or 2·12d. per grain, will save much labour in calculation. In some countries only £4 per fine ounce is allowed, in which case the table would be constructed on a £4 per ounce or 2d. per grain basis.

If the results are required in percentages the calculation is simple—30 gms. ore give ·0035 gm. gold; what will 100 gms. ore give?

Accuracy of Results.—The chief sources of error in this assay are the following:—

(1) Inaccurate sampling.
(2) Traces of gold may be retained in the slag.
(3) Traces of gold are absorbed in the cupel.
(4) Traces of gold are volatilised in cupellation.
(5) The bead may contain base metal (affects the silver).
(6) The silver, on parting, is retained in traces entangled in the gold.

With careful work, Furman estimates the average loss in the crucible assay as ·3% of the total gold present; that is, if a bead of gold after parting weighs 0·005 gm., the probable amount of gold present is ·005 gm. $+ \frac{·005 \times 3}{1000}$ = ·005 + ·000015 = ·005015 gm. This, for most technical purposes, is a high degree of accuracy, and leaves little to be desired. Loss (1), inaccurate sampling, may with care and practice be reduced to a minimum. Losses (2) and (3) may be almost completely recovered by assaying the slag and cupel, which are ground up and fluxed with litharge reducer and a little fluor spar. Loss (4) is reduced to a minimum in the case of clean ores by careful cupellation, and as far as the gold is concerned is almost negligible. Loss (5)

barely affects the gold present unless much copper is alloyed with the gold. As in the case of blister copper, traces of gold probably are lost on solution in nitric acid. Error (6) is on the other side, and to some extent counterbalances the previous losses. If, however, the gold be broken up on parting, this gain, as shown by the following experiments, is practically nil.

Gold ·01 gm.
Silver ·06 gm. } Average of six trials, gold practically unchanged.

Pure gold was taken, alloyed with six times its weight of silver, and parted as usual in porcelain cups.

Method No. 2—Scorification.

The applicability of the various methods will be discussed later; here the methods themselves are described.

The ore taken is of the same nature as before and is fairly rich, that is, it is supposed to contain over 1 ounce gold per ton.

Principle of the Assay.—The silica is fluxed by litharge forming lead silicate, and the iron oxide, if present, is partly fluxed with borax glass. The litharge is obtained by the oxidation of metallic lead, part of the lead used being thus oxidised and part remaining to collect the gold and silver. The subsequent treatment of the button thus obtained is the same as that described under the first method.

Apparatus.—The muffle furnace, scorifiers, pulp scales, balance, weights, and the usual accessories.

Reagents.—Granulated lead, borax glass, and the usual parting acids. (The granulated lead may be purchased or prepared by pouring melted lead into a stout wooden box and rapidly agitating the box *just* as the lead solidifies. The product is sifted and the coarse material is re-treated.)

Details of the Assay.—Fire the muffle to a bright red, and weigh in duplicate the following charge—

Ore, ...	10 gms.
Granulated Lead, .	50 „
Borax Glass, . .	2 „

Take approximately half the lead, and with it mix the ore, and transfer the mixture to a 3 inch scorifier, and add the remainder of the lead as a cover. Part of the borax glass is now added on top, and the remainder may be used during the operation, should the slag become too thick.

Having charged the two scorifiers, transfer them to the muffle, close the doors till the lead melts and the ore floats on the surface. Open the doors and keep up the temperature to fuse all the material. A ring of slag forms, which gradually closes in. Add a little borax glass if the slag appears pasty. The temperature is kept constant till the slag ring closes in and almost covers the surface of the molten lead. The temperature should now be raised for a few minutes to thoroughly liquefy the slag. The scorifiers are now removed and the charges poured.

When cool, the button is detached from the slag, cupelled, inquarted, parted, and the gold weighed as before.

Calculation of Results.—The calculations given in No. 1 Method apply here.

Accuracy of Results.—The *general* applicability of this method will be discussed later on; here it is considered solely as applied to clean gold ores. For rich ores (30 dwts. and upwards) this method is more convenient than and quite

as accurate as the Crucible method, provided the slag be re-treated when dealing with ores over a few ounces. (The slag is ground and re-scorified with fresh lead). For poor ores the method is not convenient, as with 2 dwt. ores 6 or 8 scorifications must be done, and the resulting buttons are then scorified into one. It is obvious that the gold obtained must be very carefully weighed, as any error in weighing is multiplied to a greater extent than in the crucible assay; also that care must be exercised in sampling when a small quantity of ore is taken for assay. The student is advised to check this method against the Crucible method on the same ore used in No. 1. If the ore is under 1 oz. let him perform four scorifications, and combine by scorification each pair of buttons. The results so obtained should agree in ounces and pennyweights, and not differ by more than 6 grains.

(*b*) **Basic Oxidised Ores.**—These ores are generally the decomposition products of sulphide ores, and such ores generally contain a high percentage of hematite or limonite. Other ores coming under this head contain calcite, dolomite, etc.

Principle of Assay.—Any silica present is fluxed by ferrous oxide (forming $FeSiO_3$), and sodium carbonate (forming Na_2SiO_3), and calcium carbonate (forming $2CaO, SiO_2$). The ferric oxide present is reduced to ferrous oxide by charcoal powder. The proportion of borax used increases with the amount of iron oxide present. With very basic ores, silica, in the form of sand or glass (free from gold and silver), must be added, or the crucible may be eaten through. Litharge is now unnecessary to form double silicates.

The calculation of the quantities of fluxes theoretically required is too intricate to go into here, but the student who has obtained some insight into the methods of calculating blast-furnace charges can with a fair degree of accuracy apportion the fluxes to a given ore.

The charges alone will be given, the details of the operation being similar to those already given.

Instructions for Assay.—Weigh out in duplicate one of the following charges, according to the nature of the ore:—

Ore contains	30% to 50% Fe_2O_3,	over 50% Fe_2O_3.
Ore . .	30 gms.	30 gms.
Soda .	20 „	10 „
Litharge .	25 „	30 „
Charcoal .	2 „	4 „
Borax .	20 „	25 „
Silica		10 „

Fuse, cupel, part, etc. as usual.

Calculations, Accuracy, etc.—Little additional need be said here. If the student judiciously proportion his fluxes and ore, he should obtain results very closely approaching in accuracy those previously discussed. Authorities state, for instance, that the loss of gold in the Crucible method averages ·3%, but the student must remember that different operators attain to different degrees of accuracy, hence the necessity of carefully checking the accuracy of each portion of his work. On this point he is advised to consult Rose, Furman, Roberts, Austen, and others. The accuracy of his work as a whole he may check as follows:—Repeat the assay, but add to it a small bead of *pure* gold, the weight of which is taken. The result of this assay should equal that of the previous, plus the weight of pure gold taken. Any difference will give him some idea of the total accuracy of his work. Or (what is better) instead of the ore he may take glass powder, add gold dust, and conduct the assay.

(*c*) SULPHIDE ORES.

These ores may contain silica, gold, silver, and a considerable percentage of sulphides of iron, copper, zinc, arsenic, etc.

(1) Ores containing Iron Pyrites (FeS_2).

(*a*) Less than 20% FeS_2.

(*β*) More than 20% FeS_2.

(*a*) Gold Ores containing less than 20% FeS_2.

The Iron or Nail Method.

Principle.—Sufficient soda is added to flux the silica, and an excess to give a fluid alkaline slag in which the FeS formed by the iron introduced and the sulphur in the pyrites may dissolve. The sulphur present acts to a certain extent as a reducer. One gram FeS_2 is capable of reducing 8 gms. Pb.

Therefore if a button of 15 gms. is required, this would be obtained if about 2 gms. FeS_2 were present, that is, if 30 gms. of ore are taken, the ore must contain 2 gms. FeS_2, or about 6% FeS_2. If 50 gms. ore, about 4%. When less than this of FeS_2 is present, charcoal or argol is added as a reducer. If more is present, nails or iron wire is added. A preliminary assay will give the necessary information.

Borax is added to flux any FeO that may be formed by oxidation of FeS.

Apparatus and Reagents.—As before, with the addition of 4 nails or loops of wire.

Details of the Assay.—Weigh out in duplicate the following charge, the ore being sampled and crushed as before.

Ore, . . .	30 gms.
Red Lead, . .	25 ,,
Soda, . . .	30 ,,
Borax, . .	10 ,,
Charcoal, . .	1 gm. to 0·0 gm. according to trial.

Note.—Red lead is used in preference to litharge on account of its higher oxidising power.

As a preliminary, mix charge and fuse one charge, using no charcoal. Examine the resulting button, noting its weight. If too small a button is obtained, add sufficient reducer to bring down the required lead; if too large, add another nail or wire loop.

The assay proper is conducted as before, the fire being kept at a dull red for 5 to 10 minutes, and then at a bright red for another 20 minutes. The nails or wire are washed and removed and the charge poured, and the remainder of the operation and the calculations are conducted as usual.

Accuracy.—From data available it seems that this method gives good results when applied to ores containing less than about 20% FeS_2. Only a certain amount of FeS can be dissolved in the slag, and any rise above this saturation point results in the formation of a regulus in addition to the lead button. The addition of more iron only partially remedies this evil, so that the scope of the method is limited.

(β) Gold Ores containing over 20% FeS_2.

The 'Roast' Assay.

Method.—The ore is carefully roasted, ferric oxide being formed. The roasted ore is then treated as a basic ore.

Apparatus, Reagents, etc.—As before, with the addition of roasting appliances.

Details of the Assay.—Weigh out two charges of 30 gms. ore each. Transfer to 10 cm. roasting dishes and carefully roast 'dead,' as before described (see Roasting). In this process loss by careless stirring must be avoided. This roasting will take from 40 to 60 minutes for 30 gms. ore.

Flux each charge of roasted ore with the charge given for basic ores, conducting the operation as there described.

The student is advised to assay the same ore by the Nail method, and compare the results.

Accuracy.—For the ores considered this is the most accurate of all methods given in the various text-books. Though not so quick as the Nail method, the results are higher and more reliable. Clean buttons are obtained, and therefore clean cupellation, though in the case of the nail assay but little loss is experienced if an impure button is treated at the outset with a high temperature in the muffle furnace.

Note.—These and other sulphide ores under certain conditions are quickly and accurately treated by scorification, the roasting being performed in the scorifier (see Silver Sulphide). Some assayers use the Nail Method on all sulphide ores. Any regulus obtained should be scorified with the lead button.

(2) CUPRIFEROUS SULPHIDE ORES.

These ores frequently are poor in gold and silver, and contain a fair percentage of copper, besides iron, sulphur, silica, etc.

The outlines of two methods are here given. If the student be pressed for time, he may omit these assays for the present, as the matter will be treated again to some extent under "Mattes."

The Roasting Method.—The ore is roasted as before described. As copper will be reduced into the button, sufficient lead must be added to give the proportion of 15 lead to 1 copper, or if this give too large a button for cupellation, it must be scorified (once or twice, according to the quantity of copper present) at a *low* heat. The following charge answers these requirements:—

Ore,	30 gms.	
Red Lead,	60 „	
Soda,	30 „	
Argol	4 „	(according to copper present).
Borax,	10 „	

Accuracy.—With care, good results are obtainable. A comparison of the accuracy of the Fire and Wet methods as applied to the estimation of gold in copper products will be given when treating Mattes and Blister Copper.

The Combination Method.

Principle.—The copper is first removed by treatment with acids, and the residue is then treated as an ordinary ore.

Apparatus.—Porcelain basins (15 cm.) and covers, filtering apparatus, etc. The usual assay outfit.

Reagents.—Fuming nitric acid, hydrochloric acid, and the usual assay reagents.

Details of the Assay.—30 gms. ore are cautiously dissolved in fuming nitric acid. The solution is warmed to drive off nitrous fumes, and diluted with water. Hydrochloric acid is added to precipitate the silver. Decant through a double filter paper. Wash by decantation. Place the filter paper in the porcelain basin, and dry on a sand bath or hot plate. Ignite the paper. Mix the following charge:—

Residue,	—	gms.
Soda,	20	„
Red Lead,	30	„
Borax	10	„
Argol,	3	„

Fuse and treat as usual.

Accuracy.—From the scant data available, and from analogy, it would seem that this method, though giving cleaner buttons, is not quite so accurate as the All-Fire method when properly conducted. Opinions on this matter, however, differ, and judgment may be reserved till further research gives sufficient data.

(3) ANTIMONIAL ORES.

Method employed.—Since both the sulphide and oxide of antimony are volatile, and may on volatilising carry off some gold, other methods of oxidation than roasting are resorted to. The antimony may be removed by wet methods (solution in HCl and $H_2C_4H_4O_6$), or partial or complete oxidation by nitre may bring about the desired effect.

The method here described is that of *partial oxidation by nitre.* The remainder of the antimony is oxidised by the litharge or red lead.

Apparatus, Reagents, etc.—As before.

Details of Assay.—Reduce the ore (containing 50% or more of stibnite), and pass the final sample through an 80 sieve. Weigh out the following charge in duplicate:—

Ore,	36	gms.	
Red Lead,	60	„	
Soda,	25	„	Salt cover
Borax,	10	„	
Nitre,	25	„	

After thorough mixing transfer the charges to G crucibles. Fire at a dull red, and when effervescence ceases slightly urge the fire, withdraw the crucible, and swirl the slag round the sides by slightly rotating the crucible. Pour the charge. The button obtained should weigh about 25 gms. If the button is brittle it indicates insufficient nitre, and this must be readjusted in a fresh trial. Some experience is necessary in running this assay, but by an intelligent modification of the charge given good results may be obtained. The buttons are cupelled, etc. as usual.

Accuracy.—It is difficult to ascertain which of the methods cited is the most accurate. The authors cannot find sufficient data to decide the point, and for the present the student may safely assume that with practice and care the results obtained are at least satisfactory.

(4) ARSENICAL ORES.

Method adopted.—These ores may be treated either by the Nitre method just given or by a modification of the usual Roasting method. This latter is here described.

Apparatus and Reagents.—As before.

Details of the Assay.—Weigh out two charges, each of 30 gms. ore (containing a fair percentage of arsenical pyrites), and transfer to roasting dishes. Commence the roast at a temperature below a visible red. Gradually increase the temperature, continuing the roast as usual. Remove when apparently completely oxidised, and mix with 5 gms. charcoal and roast till all the charcoal is burnt away.

The residue is now treated as a basic ore.

Accuracy of Method.—Much controversy exists regarding the roasting of arsenical ores. With the precautions mentioned losses are reduced to a minimum, but research has yet to show the exact value of this minimum.

The application of the scorification process to these and antimonial ores will be considered later on. The method chosen will give the student experience in the roasting of arsenical ores. With careless roasting, besides losing gold by volatilisation, he will find that arseniates are formed which are remarkably stable even at a high temperature.

(*c*) TELLURIDE ORES.

Whether the so-called tellurides of gold are true chemical compounds or not is doubtful, and recent research, though not clearing away all doubt, indicates a strong probability of their not being true chemical compounds. It is sufficient, however, for the student's present purpose to bear in mind that unless he is careful in choosing a suitable method and in carrying it out, he is almost certain to under-estimate the gold in the ore.

Method adopted.—Certain writers (Fulton and Smith) advocate the Crucible method as alone suitable; others (including Furman) recommend the Scorification method with the addition of litharge; others again hold that either method gives good results provided the ore be reduced fine enough (120 mesh). The method recommended by Chas. H. Fulton and Ernest A. Smith is here given with slight modifications.

The ore is not roasted and a large excess of lead oxide is used, converting tellurium to telluric acid, forming tellurate of lead. This excess of lead oxide prevents the TeO_3 volatilising.

Details of Assay.—Pass the final sample of the ore through a 120 sieve. Weigh out in duplicate one of the following charges, according to the richness of the ore.

Rich Ore Charge.		Poor Ore Charge.	
Ore,	10 gms.	Ore,	30 gms.
Red Lead,	100–150 „	Red Lead,	30–120 „
Soda,	50 „	Soda,	30 „
Silica,	5–10 „	Silica,	5 „
Argol,	4 „	Borax,	10 „
		Argol,	4 „

The red lead is varied according to the tellurium present. Mix thoroughly and cover with salt. Fuse slowly at first, gradually raising the heat to a

bright red. Time of fusion, about 40 minutes. With strange ores always re-treat the slag. Cupel the resulting buttons at a low temperature.

Accuracy.—From what has been stated, the student will conclude that some doubt exists regarding the suitability of the various methods given. Further research is necessary, but for the present the student must accept the results obtained as being of a fair degree of accuracy.

(2) PRODUCTS.

By these are meant materials other than ores. Such materials are generally produced at some stage or other in the extraction of gold from its ores. Out of the many gold-containing products the three here considered are *mattes*, *blister copper*, and *gold bullion*.

(*a*) MATTES.

These are very variable in composition. The matte here considered—a copper matte—consists of sulphides of copper and iron, gold and silver, and small quantities of sulphides of other metals such as lead, antimony, etc. The student will see that this product closely resembles the cupriferous sulphide ore previously treated for gold. The assay is again considered, on account of its great importance to the copper smelter; and as in the products considered the percentage of copper is generally much higher than in ores, special methods must be adopted to secure accurate results.

Method of Assay.—That there is room for improvement in the assay of these products the student will admit when he has laboriously conducted the operations necessary. Briefly, it may be said that the accurate methods are tedious, expensive, and too lengthy for technical use. The quicker methods are inaccurate, often to a very serious degree. At present the dry or 'all-fire' method of estimating gold will be described, and under the heading Blister Copper a description of a combination method will be given, together with a summarised criticism of the various methods advocated by eminent chemists and assayers.

In the method here adopted the copper is got rid of by scorification, which with rich mattes must be repeated, borates and silicates of copper and iron being formed. When the lead button is obtained sufficiently pure by scorification it is cupelled.

Details of the Assay.—Weigh out 4 charges of the following, the matte sample being passed through an 80 sieve.

Matte, . . .	3 gms.	Cover, 40 gms.	**Lead.**
Granulated Lead, .	40 „	½ „	Borax glass.

Transfer the charges to scorifiers, adding the cover as shown. Commence the scorification at a low heat till the sulphur is oxidised, then raise the temperature and finish as usual. Pour the four charges. Replace two scorifiers (preferably new ones) in the muffle, and in each place two of the buttons obtained. Rescorify till the resulting button weighs about 15 gms. Cupel at a low temperature and treat as usual, noticing whether any copper is present in the solution on parting.

Calculation of Results.—These are calculated on the usual principles.

Accuracy of Results.—The method given is the most accurate for the estimation of gold in copper matte (but not for silver). The student will see

from the notes given under Blister Copper that perfection is yet a long way off in that estimation, and, from analogy, in this also.

(*b*) BLISTER COPPER.

This material may be taken as containing 96 to 98% copper, a few ounces of gold per ton (varies considerably with different ores), some hundreds of ounces of silver per ton, and small quantities of impurities.

Though the estimation of silver has so far not been considered, the student will find it convenient to estimate both silver and gold when conducting the assay.

Method adopted.—Many methods have been tried and are in use. Briefly, they come under one or other of the four following classes :—

1. 'All-fire' (or dry).
2. „ „ corrected.
3. Combination (wet and dry).
4. „ „ „ corrected.

1. The *all-fire* method is somewhat similar to the fire method given for mattes. Ten portions of 3 gms. each are scorified at a high temperature, and the resulting buttons are combined by rescorification till suitable for cupellation.

2. The *all-fire corrected* method is simply the all-fire method plus an estimation of the slag loss and cupel absorption loss.

3. The *combination* method will be described.

4. The *corrected combination* method is simply the last method, corrected as before described.

On reference to American literature, the student will find numerous methods given, more especially combination methods. For the present he may estimate the gold and silver by the combination method given, and under the head '*Accuracy*' he will find a summary of the research work of some of the most celebrated American chemists.

In the method described the blister copper is dissolved in nitric acid, leaving *most* of the gold as a residue. NaCl or HCl is added to precipitate the silver. The gold and silver are separated from the copper by filtration, and then are estimated by the Fire method.

Apparatus.—Pulp scales and assay balances and weights, beakers and covers, etc., the muffle furnace and accessories.

Reagents.—The usual assay reagents, together with nitric acid and salt.

Details of the Operation.—Weigh out in duplicate 30 gms. of borings of blister copper, taking care that any fine particles are evenly distributed in the two lots (the finer portions generally differ in value from the long drillings).

Transfer each lot to a 750 c.cs. beaker. Add 100 c.cs. distilled water and 50 c.cs. HNO_3 (S.G. 1·42), and cover. When the violent action ceases add 50 c.cs. more of HNO_3 and warm till the copper is all dissolved (takes about one hour). Boil off part of the HNO_3 (taking from 20 to 30 minutes). Remove the beakers and dilute with distilled water to 400 c.cs. Run in sufficient normal NaCl solution to precipitate all the silver. Avoid large excess (test). Either stir vigorously for 20 or 30 minutes (or use air jet), or allow the precipitate to settle all night. Filter through double filter papers 15 cm. diameter, of good quality. Wash the pp. well to the point of the filter. On top of the AgCl add 6 gms. test grain lead Transfer the moist papers and pp. with lead to

2½ inch scorifiers, on the bottoms of which is spread 2 gms. of test lead, Dry and burn the papers and contents in the muffle below a dull red (takes about 20 minutes). Add a few gms. litharge and 2 gms. borax glass, fuse for a few minutes and pour.

Cupel the buttons at a low temperature (feathers). Part and weigh as usual.

Note.—The gold may be separately estimated by filtration before adding NaCl.

Calculations.—Principles and method as before.

Accuracy of Methods.—Authorities give the following:—

"**Ricketts and Miller.**"—*Fire* method, good results for gold; low for silver. *Combination* method, low results for gold; about the same for silver.

"**Furman**"—referring to mattes—gives the loss of silver by scorification as 2% to 4%. Seems to recommend the Combination method for silver, but does not state its accuracy for gold.

"**Ledoux**" (1900).—Combination method gives low results for gold, and leads one to infer that the results for silver are good. With blister copper containing 96% to 98 % copper and 1 to 5 oz. gold per ton, the gold results are ·1 to ·3 oz. higher by the All-fire than by the Combination method. He considers Dr Godshall's combination method, using H_2S to precipitate silver, good for silver but low for gold.

"**Van Liew.**"—Summarises "Ledoux's" earlier work, in which carefully sampled blister copper was submitted for assay to many leading American chemists with the following results:—

Silver by **Scorification.**—9 chemists reported, with a variation of 6·06% on an average of 159·36 oz. per ton.

Silver by **Combination** method.—15 chemists reported 16 results, with a variation of 8·24% on an average of 154·9 oz. per ton.

Briefly, 19 chemists give 25 determinations, using these two methods, with a variation of 8·25%, or an average of 156·3 oz. per ton.

Silver by **Corrected Scorification.**—5 chemists reported results; average before correction 151·95 oz., after correction 158·96 oz. That is, uncorrected there is at least a loss of 4·43% silver.

Silver by **Corrected Combination.**—4 chemists reported results; average before correction 156·26 oz., after correction 160·30 oz. That is, uncorrected there is an average loss of at least 2·52%.

Gold.—20 chemists reported 26 determinations by the various methods, with results varying from ·501 to ·205 oz., averaging ·307 oz., with an extreme variation of 96·4% of the average.

10 chemists reported by scorification, averaging ·362 oz.

16 chemists reported by the Combination method, averaging ·283 oz.

That is a loss of 21·8% gold by the Combination method, assuming ·362 oz. to represent 100%.

Briefly, the uncorrected Scorification method gives a loss of over 4·43% silver. The Combination method gives a loss of 3·0% silver, and 21 8% gold. Van Liew then gives a method (combination) giving an increase of 6·75% gold on the older Combination method (*N.Y. Engineering and Mining Journal*, April 1900). Yet, from Ledoux's figures, quoted by Van Liew, there must still be a loss of about 17% as compared with the All-fire method.

The above results have been given in some detail, to show the student the necessity of ascertaining the degree of accuracy attained in such work, and with the hope that they may lead him to take part in the excellent work done in this direction by American chemists. Such research must eventually result in accuracy combined with speed.

(*c*) THE ESTIMATION OF GOLD IN GOLD BULLION.

Various grades of bullion are met with—rich in gold and poor in gold; gold alloyed with silver, or silver and copper, or silver, copper, and zinc; or gold with silver, copper, lead, and zinc. For full information on this subject the student is referred to Rose, Beringer, Furman, and Ricketts and Miller.

Here the student is asked to determine the gold in standard gold coinage which contains 916·6̇ parts gold per 1000, that is, its 'fineness' is 916·66. When the student attains to the necessary degree of accuracy in this assay, he may then proceed with the estimation of gold in base bullion as described in the works mentioned, provided he has the spare time, which is not likely unless he extend his three years' course to four as advised.

The composition of the English half-sovereign is as follows:—

Gold, 916·6̇ parts; silver, nil; copper, 83·3̇ parts.

Method.—A certain weight of the coin* is taken, and sufficient silver is added to bring the proportion of the *total* silver present to the gold as 2·5 to 1. The gold and silver are wrapped in sheet lead, cupelled, the button flattened, rolled up, and parted in nitric acid, and the resulting gold weighed. Any losses are estimated by running along with the assay a 'check' made up of *pure* gold, silver, and copper. The error so found is allowed for.

Apparatus.—The assay balance, pulp scales, weights, a fine file or scissors, the muffle furnace and accessories, a thermometer and beakers (or the special parting bulbs), bullion rolls.

Reagents.—Pure gold, pure silver, pure copper, test lead, and the two parting acids.

Details of the Assay.—As a high degree of accuracy is required, the balance must be in perfect adjustment, and the bullion weights used must be checked, as was done with the weights used in gravimetric analysis. Scrupulous care must be exercised in keeping all apparatus, including the operator's hands, clean. It is only by scrupulous care in every step, combined with intelligent work, that a high degree of accuracy can be obtained.

Take a 'half-sovereign' piece and pass it through the bullion rolls till of the thickness of an ordinary visiting card.

Place in the right-hand pan of the balance the half-gram weight. This weight in a bullion set is marked 1000, and from it the weights range down to $\frac{1}{10000}$. Thoroughly clean the rolled coin by brushing. Cut off with a pair of scissors (holding the clean gold in a pair of forceps) about one-sixth of the coin, letting the piece fall on a clean sheet of glazed paper. Transfer this piece to the left pan. Slightly release the beam, and it will be seen that the piece is too heavy. Arrest the beam. Remove the piece with the forceps and clip off a thin shaving. Again try the weight, and again clip if necessary till nearly the correct weight. The final adjustment is now made by firmly gripping the piece with the forceps in the left hand and gently applying a *fine* file with the right hand. In cold weather take care that the breath does not condense on the gold or balance and weights.

The student will find considerable difficulty in perfectly adjusting the gold to the weight. If time be valuable, let him note down the weight when nearly adjusted (*e.g.* 1·0012). Repeat the process, obtaining a duplicate assay piece. The student has now weighed out two lots of the coin, each approximately 1·000, or ·5 gm. As a check, weigh out another piece, taking this time ·9166 of pure proof gold. (See Proof Gold. Several

* In this case, of Australian coinage, *i.e.* a gold-silver alloy.

students may combine in preparing proof gold. The outlay runs into one or two sovereigns, nine-tenths of which is recovered. The cost therefore is small.)

To each of these three lots silver has now to be added to bring the proportion of silver to gold as 2·5 : 1. In samples 1 and 2 there is already ·0834 gm. silver; therefore the silver required is (·9166 × 2·5) − ·0834 = 2·2081. In sample 3 there is required ·9166 × 2·5 = 2.2915 gms.

Weigh out, then, two lots each of 2·20 silver and one lot of 2·29 silver.

These instructions refer to Australian gold coinage alloyed with silver, but for English coinage alloyed with copper 2·29 gms. silver are required, and in the check ·08 gm. copper should be included.

Weigh out three pieces of sheet-lead (containing no gold), each weighing 6 gm. (weigh on the pulp scales). The lead used varies in weight according to the contents of the bullion (see advanced text-books). Take each piece of lead and wrap it round the butt-end of a lead pencil, dumping in the projecting ends to make a secure packet. Charge each packet as follows :—

Packet 1.	Packet 2.	Packet 3.
1·000 coin.	1·000 coin.	·9166 proof gold.
2·20 silver.	2·20 silver.	2·29 silver.

If English coinage, alter the proportions as directed.

In charging each packet, roll up the gold, etc., so that it occupies little space; then transfer to the packet and close the packet carefully, compressing it in the fingers into a roughly spherical shape.

Take three bullion cupels (these are about $\frac{3}{4}''$ diameter, and their surfaces are faced with fine sifted bone ash); place them in the muffle at a bright red heat. After five minutes examine them, and if satisfactory, replace them in a row across the muffle. Place packet 3 with the check-piece in the centre cupel, and packets 1 and 2 in the side cupels. Cupel at a bright red heat. Allow the buttons to remain in for five minutes after the cupellation has apparently finished. Remove the cupels either gradually (taking three or four minutes), or rapidly by setting a hot cupel on top of each and then withdrawing. This must be done carefully, or the button may roll round the cupel and cause loss.

When cool, carefully loosen each button on its cupel by means of strong pliers (this is easily done when only a little copper is present). Remove each button in turn, and brush off any adhering bone ash, gently tapping the edges with a light hammer—the button, turned on its edge, being held with the forceps. (This hammering is only necessary when the bone ash adheres very firmly to the button.) Replace the buttons on their respective cupels. Weigh them and note the weights.

The buttons must now be rolled out, and to secure uniform conditions they must all be rolled to the same thinness. A convenient size is 7·5 cm. by 1·2 cm. To roll out the button turn it on its edge, holding it in the forceps, and lengthen it by hitting a smart blow or two with a suitable hammer, the face of the

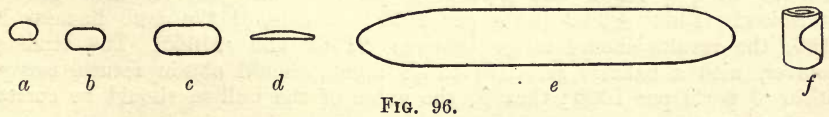

Fig. 96.

hammer and anvil being brightly polished. Now set the button on the anvil, with its original base down. Flatten to about ·75 cm. in width with one blow on the centre, and then draw out the two ends, slightly wedge-shaped, by blows with a slight pulling motion. Fig. 96 shows the various stages from the button

to the 'cornet':—*a*, the button; *b*, the button after lengthening; *c*, after flattening; *d*, after being drawn out wedge-shaped; *e*, the cornet.

The button is now annealed by heating to *dull* redness on a cupel in the muffle or before the foot blowpipe. It is then introduced between the rolls, which must be set *evenly* apart from end to end, the screws being adjusted till the rolls grip the button well, but not too tightly. Pass the button through, and it should be now about one inch long. Bring the rolls closer together; anneal the button and pass through again; a third rolling should bring the button to the requisite thinness.

Anneal, and with the fingers roll the slip round a thin glass rod, keeping the bottom side (the dull side) out (see fig. 96*f*). The cornet is now ready for parting. The other buttons are now treated in the same way, taking care to note which is the 'check.'

Special platinum parting apparatus being expensive, the assays may be parted in beakers or in 5 cm. porcelain cups.

Place three small beakers on a sand bath in a fume chamber. In each beaker introduce 25 c.cs. No. 1 acid (1·16). Gently heat till 80° C. is reached. Then introduce the cornets, one in each beaker. Heat to boiling, and continue the boiling for ten minutes. Take each beaker in turn, holding it by the rim between the thumb and first two fingers, and remove it, and decant the acid down a glass rod into a 'waste silver' jar. Now add to each in turn 25 c.cs. boiling acid No. 2 (1·26). Replace and boil for ten minutes. Remove and decant as before. To each add about 25 c.cs. distilled water, decant, and wash each with two further lots of about the same quantity of water. Transfer each cornet to a small porcelain crucible by sliding it down the side of the beaker with the aid of gentle tapping. Remove most of the water adhering to the cornet and crucible by a small slip of filter paper. Gently dry the cups and contents on the sand bath. Then anneal in the muffle for a few minutes. Remove, cool, and carefully weigh the three cornets. Enter the results.

Calculations.—A concrete example will show the necessary calculations. Assume that—

Assay	No. 1	weighs	·9170
„	No. 2	„	·9174
Check		„	·9172

and assume also that you did not know the exact amount of gold in the coin.

Then the check has gained in weight ·9172 − ·9166 = ·0006. This quantity has therefore to be subtracted from the average of the two assays which is $\frac{·9174 + ·9170}{2} = ·9172$. Then ·9172 − ·0006 = ·9166. And if 1·0012 (or other weight of bullion taken) gives ·9166 gold, what will 1·000 bullion give?

Accuracy of the estimation.—The student will see that with care and the use of checks a high degree of accuracy may be obtained. With a balance sensitive to $\frac{1}{100}$ mgm. and averaging three results, the fineness can be determined within ±0·02 parts per 1000; that is, if the true fineness be ·9166, the results should range between ·91662 and ·91658. The student, however, with a balance sensitive to $\frac{1}{20}$ mgm., should obtain results correct within ·3 parts per 1000; that is, the value of the bullion should be correct to a farthing.

Note.—When the value of the bullion is unknown, a preliminary assay is done on a small cutting, which is treated for gold and silver like a bead from an assay. The results give data for calculating silver to add and for the gold, etc. in the check (see Rose's *Gold*).

CHAPTER X.

THE ASSAY OF SILVER IN ITS ORES AND PRODUCTS.

THE estimation of silver has, to a certain extent, been considered under gold ores and products in which the gold was supposed to predominate. Here such ores and products will be considered as generally contain higher values in silver than in gold. Most gold ores contain some silver, but not enough to bring them under this head.

The two materials here considered are—

(*a*) **Silver coinage** (English).
(*b*) **Galena.**

(*a*) THE ESTIMATION OF SILVER IN COINAGE.

For practice, a convenient material to operate on is an English silver coin, which contains 925 parts of silver to 75 parts of copper by weight. The student, therefore, knows the composition of the alloy. When dealing with alloys of unknown composition the process is more complicated (see note appended).

Method.—A given weight of the bullion is cupelled with lead sufficient to remove the copper. Any loss in cupellation is estimated by a 'check' assay and allowed for.

Apparatus.—The assay balance and weights, the muffle furnace and accessories, a fine watchmaker's file.

Reagents, etc.—Sheet lead, the silver contents of which have been estimated, electrolytic copper (sheet), and test silver.

Details of the Assay.—Weigh out, as before, four lots of 1·000 each of a clean flattened silver coin, and two lots of ·925 each of test silver, and two lots of ·075 each of electrolytic copper, and six lots of 7 gms. sheet lead, the silver contents of which are known. Shape the lots of sheet lead into packets and arrange the packets as follows:—

(1)	(2)	(3)	(4)	(5)	(6)
1·000 Coin.	·925 Ag.	1·000 Coin.	1·000 Coin.	·925 Ag.	1·000 Coin.
	·075 Cu.			·075 Cu.	
7 gms. Lead.	7 gms. Lead.	7 gms. Lead.	7 gms. Lead.	7 gms. Lead.	7 gms. Lead.

Nos. 2 and 5 are the checks; Nos. 1, 3, 4, 6 the assays.

Mark six bullion cupels with these numbers and place them in the muffle for five minutes at a temperature slightly below a bright red. Examine, and if satisfactory, replace in two rows across the muffle,—first row, 1, 2, 3; second row, 4, 5, 6; the checks being in the middle. Quickly introduce the six charges.

Close the door till cupellation commences, and then open it and continue the cupellation so that 'feathers' just begin to form. It is rather difficult to obtain this heat, as the back row will be slightly hotter than the front; however, it may be closely approached by bringing the cupels forward in the muffle and keeping the two rows very close together, taking care, of course, that the charges do not freeze. When the blick (or coloured films) just disappears, close the doors for a few minutes and then remove the cupels, taking the usual precautions against the button spitting. When cool, clean and weigh the buttons, noting the results, and all details as to time of cupellation, temperature, etc.

Calculations.—Assume that the weights of the buttons are as follows:—

(1) ·9225	Back Row	(4) ·9230	Front Row
(2) ·9220		(5) ·9228	
(3) ·9221		(6) ·9231	

$$\text{Average of assays 1, 3, 4, 6} = \frac{\cdot 9225 + \cdot 9221 + \cdot 9230 + \cdot 9231}{4}$$
$$= \cdot 9227.$$
$$\text{Average of checks, 2, 5} = \frac{\cdot 9220 + \cdot 9228}{2}$$
$$= \cdot 9224.$$
$$\text{Loss in cupellation} = \cdot 925 - \cdot 9224$$
$$= \cdot 0026.$$

Add this to the average of the assays,

$$\cdot 9227 + \cdot 0026 = \cdot 9253.$$

That is, the fineness of the bullion is 925·3.

Accuracy.—With good work, the cupellation loss should not be more than 6 parts per 1000, and on the average between 2 and 3 parts per 1000. This method, though not so accurate as the Volumetric method previously given, still is of a high degree of accuracy when checks are used. It further is of use in demonstrating to the student the necessity of careful cupellation when estimating silver.

Note.—If the composition of the coin were unknown, a preliminary lot of 1·000 is cupelled with about 10 gms. lead. The result is weighed, and an equal quantity of silver is taken for the check: *e.g.* The preliminary gives ·921 Ag. Make up checks of ·921 Ag and ·079 Cu (or other base metal if present). Then proceed as usual with the assay and calculations.

(*b*) THE ESTIMATION OF SILVER IN GALENA.

The student has already assayed this ore for lead, and by cupelling the buttons so obtained he will obtain some idea as to the silver contents of the ore; but to obtain accurate results the ore must be specially treated either by crucible assay or by scorification. The student is advised to run four assays by the one method and four by the other on the same sample and compare the results.

(1) The Crucible Assay.

The principles of this method have already been discussed. Nails are used as before, and sufficient litharge is added to give a lead button of about 15 gm.

Apparatus and Reagents.—As before.

Details of the Operation.—Weigh out four charges of sampled galena (80 sieve) and fluxes, etc. as follows:—

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Ore,	10 gms.	4 nails and salt cover.
Soda,	30 „	
Litharge,	10 „	
Argol,	5 „	

If the ore contains little SiO_2, add some clean sand. Fuse as usual. Cupel one of the buttons. Then make two checks with the quantity of silver thus found and the amount of lead in the buttons. Cupel these checks and the other three buttons as before. Note the results.

Calculation.—Suppose the heads weigh

(1)	·0054 gm. Ag	(5) ·0052	Checks
(2)	·0054 „	(6) ·0053	
(3)	·0053 „		
(4)	·0055 „		

Average of checks, ·00525.
Loss, 0·0054 − 0·00525 = ·00015.
Average of assays, ·0054.
Corrected average, ·0054 + ·00015 = ·00555 gm.
Calculate oz., dwt., grs. as usual.

Note.—These figures are purely imaginary, and simply show the method of calculation. Checks are only necessary where a high degree of accuracy is required.

(2) The Scorification Assay.

Weigh out four charges, each as follows :—

Ore,	10 gms.
Grain Lead,	40 „
Borax Glass,	½ „

For variation in practice, the student may add a 7 cm. nail to each of the first two charges. This, though not necessary, aids the desulphurisation. Place the charged scorifiers in the muffle. Close the doors till the lead melts. Open the doors; bring forward the scorifiers and allow the roasting to proceed. When the sulphur is mostly removed, proceed as usual.

Cupel the buttons, using checks for silver loss. It is advisable both here and in the previous case to part the silver beads obtained, and deduct any gold that may be found.

The methods of calculation are the same as before. The accuracy of the method for silver is high, probably higher than the Crucible method. Certainly for rich ores this method is preferable to the Crucible.

The Limitations of the Crucible and Scorification Processes.—It is somewhat difficult to define exactly the scope and accuracy of each of these methods. Authorities differ, and the precise limits of each method remain yet to be defined by further research and collection of data. Wherever the student is in doubt let him try both methods, using corrections and checks. Then, provided he can sample with a fair degree of accuracy, let him adopt the method which gives the higher results. He must, of course, satisfy himself that the 'gold' he obtains is gold, and not gold + silver or copper; and so with the 'silver,' it must be practically pure silver. The following tabulation, though open to criticism, roughly attempts to summarise the scope of the two methods, and also their accuracy.

Crucible Assay.

Gold Ores.

Range for 30 gms. assay,
30 dwts. to *5* dwts.
Range for 60 gms. (combined),
scorify buttons together.
5 dwts. to *1* dwt.
Below 1 dwt.
Further combination of buttons is required, and for very small quantities the special methods used by the investigators of the traces of gold in rocks and minerals must be used.

Silver Ores.

Range for 30 gms. assay,
10 ozs. to *10* dwts.
Below this lower limit it is unnecessary to go, as such ores are valueless. Therefore this method has no special claim for silver.

Scorification Assay.

Gold Ores.

Range for 5 gms. assay,
30 dwts. and upwards.
That is, *all rich gold ores except Tellurides;* and some assayers claim good results for this method even with Tellurides.

Silver Ores.

Range for 5 gms. assay,
10 dwts. and upwards.
That is, *practically all silver ores of any value.*

CHAPTER XI.

THE FIRE-ASSAY OF COPPER IN SOME OF ITS ORES AND PRODUCTS.

This assay is presented here, not with the purpose of giving the student an accurate and handy means of estimating copper in its ores, but to give him some practice in manipulation, which, on the small scale, somewhat resembles metallurgical methods. In all modern mining fields the fire-assay of copper is replaced by the Volumetric or Electrolytic methods, both of which have been given (except the Lake Superior method. See advanced text-books).

The ore taken for assay is a clean sample of copper pyrites or copper matte.

Method.—The sulphur in the ore or matte is eliminated by roasting. The oxide thus formed is reduced to metallic copper by fusion with potassium cyanide (Ricketts and Miller).

Apparatus.—The usual scales and furnaces for roasting and fusion (Hessian crucibles).

Reagents.—Ammonium carbonate, charcoal, borax glass, potassium cyanide.

Details.—Weigh in duplicate 10 gms. finely powdered (80 sieve) ore or matte. Carefully roast as before described. Remove and mix with 1 gm. ammonium carbonate. Re-roast. Remove. Mix with 1 gm. charcoal. Re-roast. Remove. Cool. Mix with 30 gms. KCN and 3 gms. borax glass. Place in a No. 5 Hessian crucible, and cover with 10 gms. KCN, then with salt. Fuse in a bright red fire for about half an hour. Remove, and pour the charge. Cool, collect, and weigh the copper.

Calculation, Accuracy, etc.—The result, multiplied by 10, gives the percentage of copper. With clean mattes (containing no antimony, lead, etc. etc.), results accurate within 2% may be obtained; still, unless the exact nature of the matte be known, this method is too uncertain, and, as before remarked, must give place to other more accurate methods.

THE FIRE-ASSAY OF SULPHUR IN MATTES, ORES, ETC.

The method here to be given is detailed in Furman's *Manual of Practical Assaying*, and, like the estimation of copper by fire methods, lacks accuracy; yet, on account of its speed and fair approach to the practical requirements of the smelter, it may often be used to advantage in preference to the more tedious, though more accurate, estimations elsewhere described. The assay is here made to determine the amount of sulphur or matte-forming material an ore contains.

Apparatus and Reagents. The usual equipment for crucible fusions.

Details of the Assay.—Weigh in duplicate the following charge:—

Ore, ...	5 gms.
Borax Glass, . .	15 „
Charcoal, . . .	3 „
One or two nails.	

Mix well. Insert nails. Fuse in a good fire (bright red) for fifteen minutes. Withdraw the nails. Pour. When cool, carefully break away the slag from the matte button, which is then weighed.

Calculation.—This button consists chiefly of ferrous sulphide, which theoretically contains 36·3% of sulphur; but, on account of impurities present, it is better to take one-third the weight of the button as the sulphur present.

Accuracy.—As before stated, this method does not profess to any great accuracy; yet, as the time involved is only twenty to thirty minutes, it is often of service in approximately ascertaining the sulphur contents of ores to be smelted.

THE DRY ASSAY OF MERCURY ORES.

The following estimation is given as an exercise in distillation. The method has been used to advantage, being convenient and requiring little apparatus. For refined methods of distillation and absorption of the mercury by gold plates consult "Beringer," "Furman," etc.

Method.—In cinnabar the mercury is combined with sulphur. To separate these, the ore is mixed either with iron filings or quick-lime and heated in a retort. The **S** unites with the **Fe** forming **FeS**, or with the **CaO** forming **CaS**, whilst the **Hg** distils over and is collected in water.

Apparatus.—A small furnace. An iron retort 200 c.c. to 500 c.c. in capacity, and with a tube about 60 cm. long. A beaker of water and a supply of water for cooling the tube.

Reagents.—Iron filings or quick-lime.

Details of the Assay.—Sample the cinnabar ore and pass the final sample through an 80 sieve. Take 5 to 20 gms. of this ore according to its richness, and carefully mix with an equal weight of iron filings or quick-lime. Transfer the thoroughly mixed charge to the iron retort. Make a paste with whiting and water and carefully lute the edges of the retort and lid. *Firmly* fasten down the lid. Place the retort in the fire (a convenient fire is obtained by opening the stoking door of a portable muffle). Round the tube loosely wrap a piece of old blanket or other woollen cloth, and to the lower end of the tube loosely tie a small piece of rag. Under this end place a beaker with water, and so arranged that the end of the tube is about $\frac{1}{4}$ inch above the surface of the water (special care must be taken to prevent the tube dipping into the water, which may run back into the red-hot retort and cause an explosion). Gradually heat the retort to a dull red and allow a small stream of cold water to run down the cloth on the tube. Continue the distillation for 30 minutes, raising the temperature slightly at the last.

Remove the retort and the beaker in which the **Hg** has collected. Carefully remove the water from the **Hg**. Weigh on a balanced watch glass. When cool, open the retort and carefully examine the neck and tube for any small globules of **Hg**, which must be collected and weighed.

The necessary calculations are self-evident.

Accuracy.—Many data are not available, but the author has obtained results on ores between 10% and 30% **Hg** accurate (as checked by wet methods) to about one unit. This, again, is another of those methods which, though not of a high degree of accuracy, are yet valuable on account of their convenience, and further because the results so obtained often correspond very closely with those afterwards obtained in metallurgical operations.

SECTION II.

TECHNICAL ANALYSIS.

In this section eight chapters are given, each dealing with one or more technical methods of analysis. The typical technical method should be quick, accurate, and inexpensive. Accuracy may to some extent be sacrificed in favour of speed when the quantity and effect of such inaccuracy are approximately known, yet it should always be the aim of the technical chemist to combine accuracy and speed. The past twenty years have seen great advances in technical methods, but with all the advance made it must be admitted that much still remains to be done. New methods of analysis are almost daily being brought forward and published in the current chemical and metallurgical literature. Of these methods—like patents—only a few stand the test of practice. Too often it is found on trial that their range of application is too limited, or that their claims to accuracy and speed are doubtful. This being so, the student must in his future professional work receive with caution any new method applying particularly to his special work. It is his duty to test the method from the points of view of accuracy, speed, and range of application. Under this latter point he must test the effect of the presence of various impurities on the accuracy of the results. If these results are satisfactory, he may employ the method in his daily work.

Of the methods given in the following pages it will be seen that some approach the ideal in accuracy and speed, but many of the others, though accurate, fail in speed.

CHAPTER I.

THE TECHNICAL ANALYSIS OF WATER.

Introductory.—The analysis of water varies in its methods according to the end in view, *i.e.* whether the water is to be used for drinking purposes, or for the generation of steam or other purposes in the arts. The analysis for drinking purposes, termed *Sanitary Analysis*, will not be considered here (see Sutton's *Volumetric Analysis*). When considering the suitability of a water for boiler use, the objectionable impurities may either be in suspension or in solution. In the former case they may be removed by filtration, in the latter other means must be adopted. The chemist then has to estimate the quantity and nature of the impurities present, and often is expected to

advise regarding the treatment of the water. On this latter point the student may consult such works as Phillips or Stillman on engineering chemistry. The following tabulation shows the chief impurities met with.

Suspended Impurities.	Impurities in Solution.
The nature of these is generally unimportant, as they may readily be removed by filtration.	Combined to form Soluble Salts. Bases— CaO. MgO. K_2O. Na_2O. $Fe_2O_3(Al_2O_3)$. Acids— Cl. SO_3. CO_2. SiO_2. Free Mineral Acids.

In addition to these it is sometimes necessary that the amount of oxygen in solution be determined.

Generally the **Cl** is combined as follows—first with **Na**, then with **K**, then with **Mg**, then with **Ca**. The sulphuric acid combines with the alkalies **Na** and **K** provided there is not enough **Cl** to saturate them, then with **Ca**, then with **Mg**. The carbon dioxide, after the above combinations have been made, unites with the **Ca** and then with the **Mg**. Certain mineral and artesian well waters form exceptions to this general rule.

In practice certain of these impurities form scale in the boilers. This scale generally consists of carbonates and hydrates of lime and magnesia; sulphate of lime, with some iron alumina, combined water, etc.

Other impurities have a corrosive action. Therefore, to be of service to the mechanical engineer, it is advisable to classify waters thus:—

1.	2.	3.
Non-incrusting but foaming and corroding.	**Hard or Incrusting.**	**Soft, non-alkaline, and good. Have little impurities.**
Containing **NaCl**, **KCl**, etc., Na_2SO_4, K_2SO_4, etc.	Carbonates and sulphates of **Ca** and **Mg**, etc.	Total Solids { 1–10 grs. per gal., soft. 10–20 ,, ,, ,, moderately hard. Above 25 grs. ,, hard to very hard.

Of Class 1, MgCl and $MgSO_4$ are very obnoxious. Ten grains per gallon of these impurities should condemn the water for boiler use, as in contact they are easily decomposed by iron, and rapidly corrode it.

Of Class 2, up to about 40 grs. per gallon can be dealt with by 'boiler compounds,' consisting of alkaline carbonates, but above this the added alkali is apt to cause foaming.

Of Class 3, little need be said. The figures given are somewhat relative, and what is considered a hard water in one district may be much preferable to what is considered soft in another. The figures given form an approximate standard (see Stillman). The student bearing the above points in view will now be in a position to intelligently investigate a sample of boiler water.

Method of Analysis.

An excellent *rapid* method is that of Prof. Wm. Main (see Stillman). In the method here given the alkalies are determined directly, and not by difference as in Main's method. Briefly, then, the necessary estimations are as follows:—

(*a*) By evaporation, estimate the **total solids.**
(*b*) By ignition estimate the **organic** and **volatile matter.**
(*c*) Treat the residue with **HCl**; the greater part is dissolved. In this estimate **CaO, MgO, Fe_2O_3, Al_2O_3,** and the **alkalies** (before precipitating **MgO**, or in a fresh sample).
(*d*) In the residue that still remains from (*c*) estimate by fusion the **insoluble SiO_2, Fe_2O_3, Al_2O_3,** and **$CaSO_4$.**
(*e*) The **CO_2** may be determined directly in a fresh sample or by calculation.
(*f*) The **Cl** is determined, as usual, in a fresh sample.
(*g*) The **SO_3** is determined in a fresh sample.

(*a*) **Estimation of Total Solids.**—(Suspended matter is first removed and estimated by filtration.)—Take 700 c.cs. of an average sample of the water in question, and transfer till two-thirds full to a weighed platinum basin (a porcelain dish will do in case of emergency, but is not so satisfactory). Place the dish and contents on an asbestos board, on a tripod, over a rose bunsen burner. Adjust the flame so that the water is *nearly* but not quite boiling. Continue the evaporation, adding when necessary the remainder of the 700 c.cs. When *just* dry transfer to an air bath, and heat at 110° C. till the weight is constant. Enter all weights in the note-book.

Deduct the weight of the platinum dish from that of the dish + residue. The difference is the weight of the total solids. The result is generally expressed in 'grains per gallon.' The United States gallon contains 231 cubic inches, and the British imperial gallon 277·274 cubic inches. Now, as 700 c.cs. of water were taken, the student will find by calculation on the basis of 1 gal. = 10 lbs. = 70,000 grs. that the weight of the residue in centigrams gives grains per gallon. Thus, if the residue weigh ·0412 gm., the total solids are 4·12 grains per gallon. If the results are required as so many parts per million, multiply grains per gallon by 14·285. These results are based on the British standard, and, with the required proportional alteration, are easily adapted to the United States standard.

(*b*) **Organic and Volatile Matter.**—Take now the dish and its contents and heat at a dull red till no more fumes seem to be given off and the residue is white or nearly so. Besides organic matter, **CO_2** will have been driven off by this ignition. This **CO_2** is now replaced as follows:—Add about 50 c.cs. of water saturated with **CO_2**, and evaporate nearly to dryness; again add 50 c.cs. of the saturated water and evaporate carefully to dryness. When *just* dry transfer to the air bath at 110° C., and treat as before till constant.

Weight dish + total solids = gm.
„ „ + residue = „
Difference = „ = *organic and volatile matter.*

Calculate as before to grains per gallon. Any inaccuracy that may arise through imperfect replacement of the CO_2 may be checked in the final combination of results.

(*c*) **Analysis of the Residue for CaO, MgO, Fe_2O_3, Al_2O_3, SiO_2, and Alkalies.**—Moisten the residue in the dish with a few drops of strong HCl. Add 50 c.cs. dil. HCl (E.). Evaporate to dryness, and heat at 110° C. till there is no more odour of acid fumes. Add 50 c.cs. hot water and a few drops of strong HCl. Transfer dish and contents (see that the outside of the dish is perfectly clean) to a beaker and boil for a few minutes. Filter through a small filter (5 cm.). Wash well with hot water (till no reaction is obtained for HCl). Reserve the filtrate.

Dry the filter and contents, ignite and weigh. Report as grains per gallon '*insoluble residue*,' *chiefly* SiO_2, with a little Al_2O_3, and perhaps traces of Fe_2O_3 and $CaSO_4$. For most purposes it will be sufficient to report this as *insoluble siliceous residue*. If, however, further accuracy is required, fuse this residue with carbonates of Na and K in a platinum crucible, and estimate SiO_2 contents; then, if necessary, the Fe_2O_3, Al_2O_3, CaO, etc. may be estimated. The student may with advantage omit at present this examination of the insoluble residue, and consider the results as '*siliceous matter*' *in grains per gallon.*

Whilst the drying and ignition of the insoluble residue is proceeding, the filtrate is treated as follows:—Add 2 drops strong HNO_3; boil for a few minutes to oxidise ferrous compounds. Cool slightly, and make slightly alkaline with NH_4HO. Hydrates of Fe and Al are precipitated. Boil for 5 minutes to expel part of the excess of NH_4HO. Filter, reserving filtrate (preferably through a Gooch crucible); ignite and weigh. The difference between the weight of the crucible and that of the crucible and contents represents $Fe_2O_3 + Al_2O_3$. Calculate as usual to '*alumina and iron*,' *grains per gallon.*

The filtrate is now made decidedly alkaline with NH_4HO, and an excess of E. $(NH_4)_2C_2O_4$ is added. Boil for 3 or 4 minutes. Filter, reserving filtrate (preferably Gooch). Wash well with hot water (test). If much MgO is present, the precaution before mentioned of redissolving and reprecipitating must be observed. Ignite the precipitate first over the bunsen and then over the blast till constant $CaC_2O_4 = CaO + \dot{C}O + C\dot{O}_2$. Calculate the result as *grains* CaO *per gallon.*

The filtrate from the lime is evaporated to about 100 c.cs. and excess of E. Na_2HPO_4 solution. Stir rapidly with a light glass rod for a few minutes, avoiding touching the sides. Set aside in a cool place for three hours.

Note.—To save time, the student may now proceed with the estimation of Cl, SO_3, and alkalies.

Filter through a small filter and wash well with a dilute solution of NH_4NO_3. (the "Gooch" is preferable, the NH_4NO_3 then being unnecessary.) Dry, ignite (the NH_4NO_3 in the pores of the paper aids ignition), and weigh. The ignited residue should consist of $Mg_2P_2O_7$, which contains 36·024 per cent. MgO. Multiply the weight of the precipitate by ·36024 and calculate as before, the result being *grains* MgO *per gallon.*

In the duplicate estimation the student may estimate the alkalies in the filtrate from the lime. This filtrate is divided into two equal portions (measured). One is evaporated to dryness with a few c.cs. dilute H_2SO_4, forming K_2SO_4, Na_2SO_4, and $MgSO_4$. Weigh. In the other the Mg is estimated as $MgSO_4$ (calculation), and by difference $K_2SO_4 + Na_2SO_4$ is obtained; this multiplied by 2 gives total K_2SO_4 and Na_2SO_4. By calculation this may be checked against

the results obtained by the following method :—Take a fresh sample of the water, say 700 c.cs. (see above note *re* saving of time), and evaporate in a platinum dish to about 100 c.c. Add a few drops strong HCl and then $Ba(OH)_2$ solution till strongly alkaline. Boil, filter, washing well with hot water till free from Cl. To the filtrate add $(NH_4)_2CO_3$ till a precipitate ceases forming. Boil and filter off the p'p't. Wash well and evaporate the filtrate to dryness, and heat at a very dull red to drive off NH_4Cl. This treatment removes the MgO more or less completely; but as some may still be retained by the alkaline chlorides, the residue is dissolved in a small quantity of hot water, and the treatment with $Ba(OH)_2$ and $(NH_4)_2CO_3$ repeated, the resulting solution being evaporated to dryness, and the NH_4Cl expelled at a very dull red heat. When the weight of dish and contents is constant, the result is entered and calculated to *grains* NaCl + KCl *per gallon.* If required, the NaCl and KCl may be separated as described in the chapter on the Analysis of Silicates. (For the present the student may, if his time is too limited, omit this estimation.)

In the early part of the analysis, when a residue was obtained by evaporating 700 c.cs. water to dryness, the weight of this residue was noted after incineration, and replacement of any CO_2 thus expelled. This residue (in a fresh sample) may be analysed for CO_2 and combined H_2O as before described. This estimation may, however, be omitted in a technical analysis, unless for some particular reason it be desirable that the CO_2 be determined.

Chlorine may be quickly and accurately estimated volumetrically by a standard solution of $AgNO_3$, with K_2CrO_4 as an indicator.

Take 70 c.cs. of the water in a 100 c.c. porcelain dish, add two drops K_2CrO_4 (E.) solution. Titrate from a burette with the standard silver solution (4·79 gm. pure $AgNO_3$ per litre), stirring till the colour just changes from yellow to yellowish red. The silver has a strong affinity for chlorine, and silver chromate (red) is not formed permanently till all the chlorine is combined with silver. Any that is momentarily formed is broken up thus—

$$Ag_2CrO_4 + 2NaCl = Na_2CrO_4 + 2AgCl$$

Note the number of c.cs. used, and deduct ·1 c.c. absorbed in colouring the solution. Multiply the number of c.cs. by ·001 and then by 10 (briefly, by ·01), and read the result in *grains chlorine per gallon.* Take 700 c.cs. of the water. Acidulate with 10 c.cs. HCl (5E.), and evaporate to about 200 c.cs. in a large porcelain dish. Transfer to a beaker. Heat to boiling, and add, with constant stirring, 10 c.cs. $BaCl_2$ (E.) solution. Set aside for twelve hours. Filter through a Gooch, dry, ignite, and weigh the $BaSO_4$, and estimate the SO_3 *in grains per gallon.*

Combination of Results.—These are now, for example, as follows :—

Organic, CO_2, etc.,	. .	4·413	grains per gallon.
Siliceous matter,	. .	·482	,, ,,
Fe_2O_3,Al_2O_3,	. . .	·422	,, ,,
CaO,	. . . .	3·346	,, ,,
MgO,	. . . .	1·802	,, ,,
Cl,	. . . .	·421	,, ,,
SO_3,	. . . .	1·624	,, ,,
NaCl + KCl (joint chlorides),		·782	,, ,,

Note.—The Cl in this NaCl and KCl may be partly introduced in analysis.

The student must now combine these results according to the general rules previously laid down. The siliceous matter and Fe_2O_3,Al_2O_3 remain as they are. From the total solids a fair idea of the nature of the water is obtained. These in the example quoted are low; the sample may be regarded as good. As

the Na_2O and K_2O were not separately estimated, the following example from Stillman may be taken and worked out by the student:—

	Grains per gal.	*Combined.*	Grains per gal.
SiO_2, ...	0·574	SiO_2, ...	0·574
Organic and CO_2, .	2·310	Organic, . . .	1·351
Fe_2O_3,Al_2O_3, . .	0·357	Fe_2O_3,Al_2O_3, . .	0·357
Na_2O, . . .	0·434	NaCl, . . .	0·637
K_2O, ...	0·035	Na_2SO_4, . . .	0·231
CaO, ...	1·358	K_2SO_4, . . .	0·063
MgO, . . .	0·539	$CaSO_4$, . . .	2·177
Cl, ...	0·385	$CaCO_3$, . . .	0·826
SO_3, ...	1·442	$MgCO_3$, . . .	1·134
Total, .	7·434	Total, .	7·350

The Cl is first united with Na_2O. Any balance of Na_2O is united with SO_3. (If the balance consisted of Cl, it is then united with K_2O.) The K_2O is now combined with SO_3. If any SO_3 remains it is combined with CaO; and if SO_3 still remains, then combine it with MgO; but if not, the balance of CaO is united with CO_2, and the MgO is united with CO_2, the total CO_2 thus absorbed being deducted from the item.

Organic + CO_2.—On working through this calculation, the student will notice the continuity of the method. Unless the Na_2O and K_2O are estimated, only approximate results are obtained. In many cases, however, these results are sufficient; but where the proportion of chlorine is more than a few grains per gallon, the alkalies must be fully determined.

The Hardness of Water.—Water containing certain salts of lime, magnesia, etc. in solution is said to be hard. Certain of the salts, notably the carbonates of calcium and magnesium, can be almost entirely precipitated by boiling the water. The hardness due to these carbonates is termed 'temporary hardness'; that due to compounds such as calcium sulphate, magnesium chloride, etc., which are not precipitated on boiling under atmospheric pressure, is termed 'permanent hardness.'

The temporary and permanent hardness may be determined by titration with standard H_2SO_4, which gives the temporary hardness, and followed by precipitation on boiling with Na_2CO_3 (a known volume), and titration of the filtrate with H_2SO_4 for excess of Na_2CO_3. The following method is given by most writers on this subject.

Dr Clark's Soap Test.—The student will notice that on washing his hands in a hard water a considerable amount of soap is consumed before a permanent lather is obtained; the harder the water, the more soap is consumed. The soluble stearates of sodium and potassium in the soap are decomposed by the calcium and magnesium salts, forming insoluble compounds which give no lather. The hardness of a water is generally expressed as so many grains of $CaCO_3$ per gallon.

In this estimation the following standard solutions are required—standard hard water and standard soap solutions.

Standard Hard Water.—Dissolve 1·11 gms. *pure* $CaCl_2$ in a little distilled water, and dilute with distilled water to 1000 c.cs. (measured at 15° C.). One c.c. of this solution will correspond with ·001 gm. $CaCO_3$.

Standard Soap Solution.—Castile soap may be used for this purpose, but in cold weather Phillips recommends the use of sodium oleate, about 13 gms.

being dissolved in a mixture of 500 c.cs. methylated spirit and 500 c.cs. distilled water, filtering if necessary. To standardise this soap solution run in 12 c.cs. hard water standard solution into a 250 c.c. stoppered bottle. Flll a burette with the soap solution and run in 1 c.c. at a time, vigorously shaking after each addition, till a point is reached where a permanent lather is obtained. Note the number of c.cs. 12 c.cs. of the water should take 13 c.cs. soap solution, as 1 c.c. soap solution is required to make a permanent lather with distilled water alone. Suppose, however, that only 11·5 c.cs. soap solution were required. Then to every 11·5 c.cs. soap solution $13 - 11{\cdot}5 = 1{\cdot}5$ c.cs. of water must be added. Dilute accordingly with water and spirits. Check again on the standard hard water, and re-correct if necessary.

Total Hardness.—Take 70 c.cs. of the water under examination and transfer to a 250 c.c. stoppered bottle. Titrate with standard soap till a permanent lather is obtained. Note the number of c.cs. used. Deduct 1 c.c. (necessary to bring about the reaction with distilled water). The number of c.cs. gives the hardness in degrees Clark or in grains $CaCO_3$ per gallon (equivalent). If the water takes more than 16 c.cs. soap solution, add 70 c.cs. distilled water, and proceed as before. The lather will thus form more uniformly. When the water contains a fair percentage of magnesia salts the lather forms slowly. A little experience and experiment are necessary when dealing with such waters.

Permanent Hardness.—Boil 250 c.cs. of the water for one hour, keeping up to about the same volume by additions of distilled water (boiling to expel CO_2). Cool. Make up to 250 c.c. Mix well, and pour out 70 c.cs. into a bottle, and titrate as before. The permanent hardness is thus ascertained.

The Temporary Hardness is obtained by deducting the permanent from the total hardness.

For methods of estimating the oxygen in water consult Sutton's *Volumetric Analysis.*

CHAPTER II.

THE TECHNICAL ANALYSIS OF FURNACE GASES.

In chimney or furnace gases the estimations usually made are the percentages by volume of oxygen, nitrogen, carbon-monoxide, and carbon-dioxide. The more refined methods of gas analysis are too slow for technical requirements, and are replaced by the Elliott, Hempel, or other methods. The method here to be described is that of Hempel, and differs chiefly from the Elliott and others in the design of the apparatus, the procedure in each case being the removal of constituent after constituent by certain absorbents.

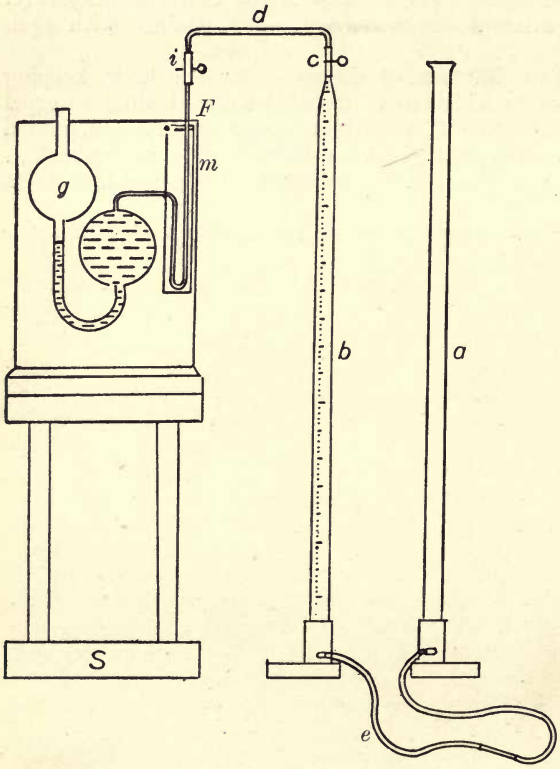

Fig. 98.

Apparatus. — Hempel's Gas Burette. — The gas burette, as shown in fig. 98, consists of two parts—the levelling tube, *a*, and the calibrated tube, *b*. This tube *b* is of uniform diameter, and ends above in a capillary tube about ·5 mm. in diameter and 3 cm. long; and at the other end the tube tapers to about one-third of its previous diameter. It is here bent at an angle and passes through the wooden upright on the base. (For the modified Winkler Gas Burette, see Hempel's *Gas Analysis*.) The tube *b* is graduated from the top down in $\frac{1}{5}$ c.cs. Total graduation 100 c.cs. The lower end of the tube *b* is connected by stout rubber tubing (4 feet) to the lower end of tube *a*, which is of even bore and ungraduated, aud fastened as before to an upright on an iron base. On the capillary tube, *c*, a short piece of rubber tubing (thick) is wired on, and clamped with a strong Mohr pinchcock. At *d* a piece of capillary glass

tube is connected between the tube and pipettes. A wooden stand, S, is used in conjunction with the burette and pipettes. One pipette must be used for each absorption. For the gases considered three pipettes are required. The simple absorption pipette is shown in place in the figure, and consists of two glass bulbs, connected with a glass tube, bent as shown, and at one end is a capillary tube and white plate; at the other end a wide tube, through which the pipette is filled and emptied. When not in use these ends are closed, one by a cock, and the other by a rubber tube and clip (or glass rod). The whole is mounted on a stand, affixed to which is a label indicating the nature of the absorbent. In the pipette the gas is agitated with the absorbent. This simple pipette will be used to absorb CO_2 by KHO. For the absorption of O and CO the compound pipette is used, as shown in fig. 99, as the reagents are acted on by the air.

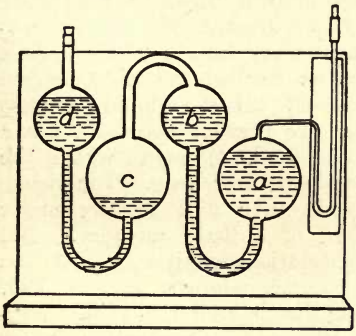

FIG. 99.

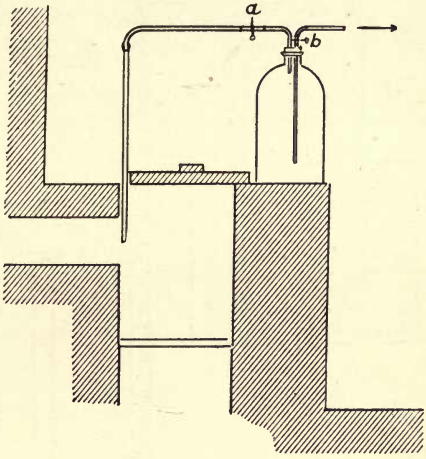

FIG. 100.

When absorbing O by pyrogallol, *a* is filled with the pyrogallol solution (see p. 282), *b* is partly filled with the same solution, *c* is nearly empty, and *d* contains distilled water.

The manipulation of the Burette and Pipettes.—The necessary determinations are as follows:—

(*a*) Carbon dioxide.
(*b*) Oxygen.
(*c*) Carbon monoxide.
(*d*) Nitrogen by difference.

(*a*) **Carbon Dioxide.**—If a furnace gas, take the sample just where the visible flame ends. In the case of an assay furnace, introduce an iron tube through a hole in the flue or through a crevice between the lid and furnace. To the outer end connect a lead or rubber pipe. Take a clean "Winchester quart" and fit it with a cork and tubes as in fig. 100.

Apply suction by an exhaust syringe till all the air is replaced by the furnace gas (for fuller details consult "Hempel"). Clamp the rubber connections at *a* and *b* and remove the Winchester and fittings. Having procured a sample of the gas, proceed to fill the three pipettes. Make a 33% solution of KHO (1 to 2). Do not use the brand "purified by

alcohol." 1 c.c. of this solution can absorb 40 c.cs. CO_2. Transfer to pipette as in fig. 98. (The "solid pipette" with rolls of iron gauze is recommended by Hempel.)

For the "oxygen pipette" prepare the solution as follows:—Dissolve 5 gms. pyrogallic acid in 15 cms. water and 120 gms. KHO dissolved in 80 c.cs. H_2O. (KHO by alcohol not to be used.) Charge the pipette as shown in fig. 99. The pipette must be so filled that when the absorbent in *a* is forced up and fills *b*, the distilled water in *c* is forced up into and fills *d*. Invert the pipette, dip the capillary in the absorbent, and fill *a* by suction. Drive the absorbent into *b* and fill *d* with water. Then by suction bring back the absorbent to the capillary.

For the "carbon monoxide pipette" dissolve 10·3 gms. copper oxide in 100 to 200 c.cs. of concentrated HCl. Then allow the solution to stand in a suitable flask filled with copper turnings till all the $CuCl_2$ is reduced to Cu_2Cl_2 and the solution is colourless. The clear solution is poured into a large beaker containing 1 to 2 litres to precipitate the Cu_2Cl_2. Decant the dilute solution; then wash into a 250 c.c. flask with 150 c.cs. distilled water. Ammonia gas is passed till the liquid becomes pale blue. To prevent access of air a stopper is used, through which the delivery and exit tubes pass. The mouth of the exit tube dips slightly under the surface of a little mercury. 100 c.cs. of the solution contain about 7·3 gms. Cu_2Cl_2. 1 c.c. absorbs 6 c.cs. CO. (Regarding the deterioration of this solution, see Hempel.) Charge the pipette as shown in the figure (99).

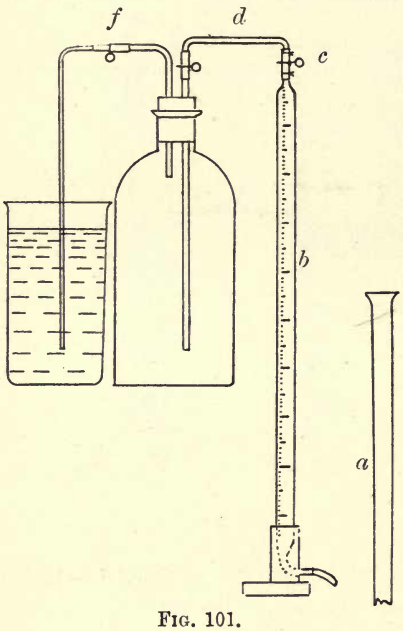

FIG. 101.

Thoroughly clean the gas burette by washing. Check by weighing (or measuring) the calibration of the burette. Fill the tubes *a* and *b* with water, raising and lowering one of the tubes till all air bubbles are removed. Join the burette to the Winchester by a glass tube filled with water by raising the tube *a*. Dip the bent arm of the Winchester in a large beakerful of water (fig. 101). Open the clamps on the Winchester. Take the tube *a* in the left hand, and firmly close the tube at *e* (fig. 98) by gripping between the finger and the palm of the hand. Pour out the water in *a*. Place *a* on the table and open the clamp *c*. The gas is now drawn into the burette. Draw in a little more than 100 c.cs. Close the clamp *c*. Disconnect the Winchester. Let the water run down the sides. Now compress the gas to less than 100 c.cs. by raising *a*. Grip the rubber tube at *e*. Set *a* on the table. Raise *b* to the level of the eyes. Slightly release the grip and allow the water to run back to 100, gripping firmly. Open *c* for a moment and the excess of gas escapes, and there remain in the burette 100 c.cs. gas under atmospheric pressure.

The absorption of the CO_2.—Set the KHO pipette on the stand. The bulb *g* is empty. Connect the pipette to *c* as shown in fig. 98, thus: fill the little tube *d* with water; then introduce capillary F which is thus filled

with water. The tube *i* is squeezed between the fingers to expel the air, and F is immediately inserted. Raise *a* and the gas passes into the pipette. With care the bubble of air introduced in the capillary should not be longer than 10 mms. When all the gas has passed into the pipette, allow about ½ c.c. of water to follow. Clamp *e*. Remove the pipette, clamp *i*, and shake for about three minutes. Reconnect. Lower *a*. Unclamp *c* and *i* and run back the gas, taking care that the KHO does not pass further than F. Clamp *c*. A better practice is to make a fixed mark at *m*, place a clamp at *i*, and always fill the tube F as well as the burette *b* with the gas. All measurements are then made with the absorbent at the mark *m*. Read the volume of the remaining gas by moving *a* till the water level is the same in both tubes. Note the reading.

(*b*) **The absorption of the Oxygen.**—The burette is now connected with the double pipette containing the pyrogallol solution. The absorption takes about 5 minutes, and must be performed by repeated agitation. The gas remaining is returned to the burette and measured as before. Note the result.

(*c*) **The absorption of Carbon Monoxide.**—The burette is now placed in communication with the CO compound pipette. The absorption here is somewhat slow, and requires frequent agitation for a period of 10 to 15 minutes. In this process a certain amount of gaseous HCl may become mixed with the gas. Transfer the gas to the burette; then for a few minutes to the KHO pipette; then back to the burette. Read as before, and note the result.

(*d*) **Nitrogen by Difference.**—In the mixture considered the nitrogen now remains, and its volume is obtained by the last reading of the burette.

The following figures are given to show the method of calculation:—

Taken, ...	. .	100 c.c. gas
Before KHO absorption, . .	100 c.c.	12·2% CO_2
After „ „ . .	87·8 c.c.	
Before Pyrogallol absorption, . .	87·8 „	7·6% O
After „ „ . .	80·2 „	
Before Cu_2Cl_2 „ . .	80·2 „	1·1% CO
After „ „ . .	79·1 „	
Nitrogen by difference, ...	.	79·1% N

When finished with each pipette, the student should note on a small label the number of c.cs. of gas absorbed. Each pipette may be used a number of times, and this practice serves as a guide when the absorbing power of the solution is in question.

When the student has finished this estimation he should proceed with another of the same sample till concordant results are obtained. It will be sufficient for the purpose of this text-book if the student master the manipulation of the simple Hempel burette and pipettes. He is referred to the *School of Mines Quarterly* for a full description of the Elliott apparatus, which is somewhat simpler than the Hempel, and to Hempel's *Gas Analysis* for modifications of the simple burette and for an elaborate examination into the accuracy of the technical *versus* the more refined methods of gas analysis. It is sufficient to state here that unless special accuracy be required for some very particular case, the methods mentioned yield very satisfactory results.

CHAPTER III.

LABORATORY ORE TESTS.

DURING the past ten years, owing largely to the growth of certain metallurgical processes, amongst which the Cyanide process is most noteworthy, the resources of the chemist have been brought to bear in determining and adjusting in the laboratory the principle and details of methods to be applied to ores on the commercial scale. In connection with the Cyanide process these tests have been developed to such an extent that it may be said that a standard series of tests is prescribed whereby the suitability of the process to any particular ore and the regulation of the various factors governing both the chemical and commercial success may be approximately determined.

The methods about to be described will give the thinking student sufficient material and ideas on which he may base equally thorough tests on other processes with which he may have in the future to deal. The metallurgical student must not be content with merely learning methods; these alone can only make a 'rule-of-thumb assayer.' He must go further, and find out why a method is used, what is its scope, and how it may be modified to suit particular cases. If he makes a habit of ascertaining such points and faithfully carries out the work laid down, preferring quality to quantity—a few methods well done and thoroughly understood, to a would-be-impressive talking knowledge of *all* the latest improvements—he will lay the foundations of a successful career.

In this place the following laboratory tests will be considered :—

(*a*) **Preliminary and Regulation Tests on Ores to be treated by the Cyanide Process.**

(*b*) **Certain Regulation and other Tests on Silver Ores.**

(*c*) **Certain Tests regarding the Chlorination of Gold Ores.**

(*a*) PRELIMINARY AND REGULATION TESTS ON ORES TO BE TREATED BY THE CYANIDE PROCESS.

With a strange ore, the first thing to decide is whether the ore is suitable or not to the process. Almost all gold ores will under certain conditions yield up some of their gold contents to a solution of potassium cyanide; but that an ore be suitable to the process, sufficient gold must be extracted at a sufficiently low cost to yield a fair profit. The student is confronted with a combined metallurgical and commercial problem. The results of the following experiments determine in most cases the applicability of the process to a given ore, and point to the most suitable conditions for success. If the laboratory experiments are favourable, a parcel of 5 to 10 tons should then be submitted to an experimental plant

for treatment on the commercial scale. Tests on a few pounds of material generally give a fair indication of what may be expected on the large scale. With a little ingenuity, a hogshead may be formed into two percolation vats, and a hundredweight of ore may be treated at once by several students. The results so obtained will approach commercial results more closely than the previous. Generally, with laboratory ore tests the extraction so obtained is somewhat higher than that in practice, but against this, the consumption of chemicals is also higher.

The following headings show the chief lines of investigation:—

Re **Suitability of Ore.**

(1) The effects of **varying strengths of solution** on the ore (30 mesh).
(2) The **consumption of cyanide**: its cause; the necessity or otherwise of preliminary neutralisation or roasting.
(3) The effects of **varying times** of treatment.
(4) The effects of **varying the fineness of ore** particles.

Re **Regulation of the Working Process.**

(1) The strength and nature of the working solutions.
(2) The determination of the gold and silver in solution.
(3) The nature of the precipitate on the zincs.

(1) The Effects of varying Strength of Solutions

A sample of a few kilos of the ore is ground to pass a 30 mesh sieve. Four vessels are prepared as in fig. 102.

A Winchester quart cut down answers well. In the bottom of each a circular piece of coarse tarred iron wire gauze is placed, accurately fitting the sides. On this is placed, a layer of coarse filter paper cut somewhat larger than the sectional area of the jar, and turned up at the edges round the sides of the glass vessel. In the neck of each jar is a cork, glass tube with rubber termination, and screw clamp. On the filter paper in each is carefully placed 200 gms. of the sampled ore. Carefully prepare a 5% **KCN** solution as follows:—Dissolve 60 gms. **KCN** (98%) in water; make up to 1 litre. Test with $AgNO_3$ (see Volumetric Analysis). Dilute as required to bring it exactly to 5%. Check the strength again. If correct, this solution is then broken down as follows:—Measure out 50, 30, 10 and 5 c.cs. of the 5% solution and dilute each lot to 500 c.cs., obtaining thus solutions of ·5%, ·3%, ·1%, and ·05% **KCN** (check with $AgNO_3$).

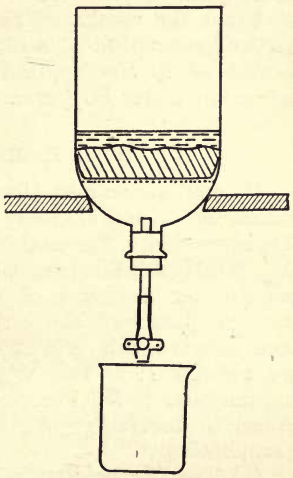

FIG. 102.

On each charge of ore carefully pour 400 c.cs. of solution, ·5% in the first, ·3% on the second, and so on. Label each jar, and enter in a note-book the conditions of the trials. Leave the clips full open and allow most of the solution to run through; close the clips and replace the solution. Set the beakers below, and slightly open the clips so that the solution will take about twelve hours to percolate through. This may be judged roughly by watching the percolation for an hour or two, and regulating the clips accord-

ingly. At the end of the twelve hours replace the solutions and continue percolation for another twelve hours. When the last of the solution has drained through, apply several small washes till no reaction is obtained for KCN (KCN being alkaline, test with litmus). Dry the residues and reserve for assay. The consumption of cyanide may be checked by titrating a sample of the solution before washing, and then returning the titrated sample. (Some silver is thus added to the solution, but this is generally immaterial.) Measure the total solution and calculate back to 400 c.cs. The student may omit this estimation at present.

The solutions thus obtained are transferred to 15 cm. porcelain evaporating basins and evaporated down to about 50 c.cs., when 20 gms. litharge are added and the evaporations finished.

Each test is treated in this way, and by a little forethought the student can so arrange operations that the whole four evaporations proceed almost simultaneously.

The residues are assayed in the usual way. Each is done in duplicate, using a 50 gm. charge. The evaporation residues are fluxed with 10 gms. soda, 10 gms. borax, and 3 gms. argol, the buttons being cupelled and parted as usual. Further checks may be made by assaying in duplicate the original ore.

The necessary calculations are simple. If residues run 3 dwts. and the gold extracted runs 7 dwts., that is a 70% extraction. There is no necessity, however, to run out the oz., dwts., grs. per ton. The percentage extraction can be determined directly from the weights of the beads.

Note.—A quicker and quite as accurate a method of treating the solution is that of Crosse, who adds $AgNO_3$ and precipitates all the Au as $AuAg(CN)_2$ (see text-books on Assaying and Cyanide, and metallurgical literature on South African practice).

From the results of these tests, the student will conclude that some one particular strength of solution gives the best results, and a fair idea may be formed as to the applicability or otherwise of the process. Generally, an extraction under 60% would be considered unsatisfactory.

(2) The Consumption of Cyanide (Feldtman's Test).

Having ascertained the amount of gold extracted, it is necessary, from a commercial point of view, to ascertain the amount of cyanide required for this extraction. The method of procedure is as follows:—50 gms. ore + 100 c.cs. ·5% KCN solution are placed in a 500 c.c. flask and agitated every few minutes for a period of fifteen minutes. Filter off some of the solution through glass wool and estimate the available KCN by $AgNO_3$. The difference between this and ·5% gives the consumption of KCN. If 2000 lbs. ore require 1200 lbs. ·5% solution, and out of this ·3% is consumed, the consumption is 3·6 lbs. per ton of 2000 lbs. As all this cyanide is not consumed in dissolving gold, the chemist then proceeds to find the cause of the consumption.

(*a*) Test for **acidity**, which may be either '**soluble**' or '**latent.**'

To determine 'soluble' acidity, agitate 10 gms. ore with 50 c.cs. water; filter and wash till free from acid. Titrate with $\frac{N.}{10}$ NaHO, indicator litmus. Note the number of c.cs. soda used.

To determine 'latent' acidity, add to the residue in a flask a measured excess of $\frac{N.}{10}$ soda (NaHO). Agitate for five minutes; let stand five minutes.

Filter and thoroughly wash. Titrate solution with $\frac{N.}{10}$ H_2SO_4. The difference between the c.cs. $\frac{N.}{10}$ H_2SO_4 and the c.cs. $\frac{N.}{10}$ NaOH give the amount of $\frac{N.}{10}$ NaOH neutralised by the latent acidity.

Soluble + latent acidity = total acidity. Calculate the amount of CaO necessary to neutralise the total acidity. Proceed with another shaking test, using the same quantities as before plus about 50% more than this theoretical quantity of lime. Besides neutralising acidity, the student should note that CaO breaks up certain double cyanides of metal and potassium, setting free potassium cyanide. If the consumption of cyanide is still excessive, proceed to test for the following (amongst other) obnoxious substances (cyanicides), soluble iron saits, soluble sulphates, copper and antimony compounds.

At present the student need only apply qualitative tests for these substances.

If tellurium be present, grind a sample of the ore to pass through a 100 mesh sieve, and carefully roast 'dead.' Then proceed with fresh extraction and consumption tests.

(3) The Effects of varying Times of Treatment.

Other things being satisfactory, and it having been ascertained that a certain strength of solution gives the highest results, it is a matter of much importance that the time of treatment be not too prolonged. On the commercial scale, 3 days may be considered an average time of treatment for sands.

Conduct three tests under the best conditions as previously ascertained—one for 2 days, one for 4 days, and one for 6 days. Note the results. It does not follow that if the 6-day treatment gives the best extraction it must necessarily be adopted; the gain in extraction, if any, may be more than counterbalanced by the loss in time.

If time permits, the student may try a few tests with so-called accelerators such as Na_2O_2, O, compressed air, bromo-cyanide, etc. These are supposed to shorten the time of treatment and to increase the extraction. Though applicable to some ores, it cannot be said that they are as yet generally successful.

(4) The Effects of varying the Fineness of the Ore Particles.

This may be a point of much importance when considering the cost of ore reduction. Test as usual under the best conditions three lots, one of 20 mesh, one of 40 mesh, and one of 100 mesh. Note the extractions.

Further refinement may here be necessary, as the material passing a 20 sieve is very uneven in grade, and much of it would pass a 40 sieve; however, for the present purpose the experiments given yield some information on this important point. Again, it may be necessary to separate 'mineral' and 'sand,' and consider each separately as a distinct ore.

Tests for the Regulation of the Working Process.

When the preliminary trials have resulted in success, a permanent plant is erected. The chemist responsible for the management of the works must not now consider that his experimental work is finished The process, if the highest results are expected, must be continually regulated to meet variations in

conditions that may arise. The chemist has to make many determinations and trials, of which the three quoted are examples. These are not here given in full. The ground has been partly covered already. For further information *re* the estimation of cyanides in complex solutions, consult the summary of the work of the leading South African chemists, as given in Sutton's *Volumetric Analysis*. *Re* the determination of gold in solution, the student may, if time permits, check his former method of evaporation by the Crosse precipitation and filtration process. *Re* the nature of the zinc precipitate, the student's knowledge of qualitative and quantitative analysis will be of service. He must in practice ascertain the influence of varying strengths of solution on the nature and completeness of precipitation. These few points out of many have been touched on to show the scope of work required in this branch. The student whose foundations in qualitative and quantitative work are well laid may with fair probability of success attempt such work; without such foundations, his services will be of little or no value when most needed.

(*b*) CERTAIN REGULATION AND OTHER TESTS ON SILVER ORES.

After a silver ore has been roasted with salt it may be necessary to determine the percentages of Ag_2SO_4 and AgCl formed. Three operations are necessary.

(1) Assay by scorification (in duplicate) the roasted are. This gives the total Ag present.

(2) Weigh out two lots of 5 gms. each of the roasted ore. Place in beakers. Add to each 100 c.cs. water; boil for a few minutes. Decant. Repeat the boiling with fresh water and decant till no more silver is dissolved (test with H_2S or Na_2S). Dry and scorify the residues.

Total Silver—Silver here found = Silver existing as Ag_2SO_4.

(3) Prepare a 20% solution of $Na_2S_2O_3,10H_2O$ ('hypo'). Weigh out two lots of 5 gms. each of roasted ore. Transfer to filters. Leach out Ag_2SO_4 with water and then the AgCl with the hypo solution till no more AgCl is dissolved (test). Dry and scorify the filter papers and contents.

Total Silver.—Silver thus found = Silver as AgCl and Ag_2SO_4. Silver as AgCl and Ag_2SO_4 – Silver as Ag_2SO_4 = Silver as AgCl.

Note.—Unless the Ag_2SO_4 be first leached out with hot water the AgCl cannot be properly estimated by hypo, but where but little Ag_2SO_4 is present this operation may be omitted in practice.

(*c*) CERTAIN TESTS REGARDING THE CHLORINATION OF GOLD ORES.

Here, as with the Cyanide process, the chemist may be called on to give an opinion as to the suitability or otherwise of the chlorination process to a certain class of ore. Laboratory tests give considerable information regarding the chemical aspect of the problem. These must be supplemented by larger trials to form a definite idea as to the commercial success of the process, remembering that to be a commercial success the chemical extraction must be, as a rule, high (say above 60%) and the cost of treatment low. As the chlorination process is contemplated when certain other processes fail, the nature of the ore is generally somewhat complex, sulphides of various metals usually being present. Roasting is generally necessary. The following tests may therefore be applied to the ore:—

(1) Assay the ore in duplicate by the crucible or scorification process (if rich).

(2) Roast about 400 gms. of the ore + 10 gms. NaCl in an iron dish, carefully stirring and continuing till 'dead.' Note the loss in weight. The ore has now to be treated with a solution of chlorine, which may be prepared either as before described (see Gases) or as follows. Mix in a wedgwood mortar 100 gms. roasted ore and 4 gms. dry bleaching powder. Transfer to a strong Winchester quart bottle. Add sufficient warm water to bring the pulp to the consistency of thin mud. Close the mouth with a rubber stopper, tied down immediately on adding 100 c.cs. of 3% H_2SO_4 solution. Wrap in a piece of sacking to prevent accident in case a weak bottle bursts. At the end of every fifteen minutes or so agitate for a few minutes. Continue intermittent agitation for four hours. Carefully remove the stopper and *cautiously* smell the contents. If there is no smell of Cl add more bleaching powder and sulphuric acid, and continue for another four hours. If satisfactory, add water, agitate, and decant through a large filter, repeating till all the ore is on the filter paper and the Cl solution is all washed through (test).

Dry the residue and assay in the usual way. Calculate back the value to the unroasted ore. The percentage extraction is thus obtained. As a check on this, precipitate the gold in the solution by ferrous sulphate. Filter; dry the paper and contents, and scorify.

The student will see that these tests could be carried much further if necessary. It may be that an undue amount of chlorine is consumed. The cause of this must be discovered. More salt might be added to the roast. Or again, a series of investigations on variations in time and method of roasting may be of commercial value. No definite line of investigation can be laid down for all ores, and the chemist must be sufficiently original to modify his mode of attack according to circumstances. Above all, he must never assume that certain reactions will occur in a given case, and therefore neglect experimenting in a certain direction. In attacking any problem he must thoroughly prove every assumption; to be on the safe side, he will doubt his methods and materials, and he will have the courage, or rather honesty, to state his results, even if they seem to reflect on his manipulation or methods. From results of analysis only too frequently published, the student is led to conclude that in a complex analysis the results combined give the 100% aimed at. If the student will consult the series of articles previously referred to in the *Chemical News* on the Analysis of Silicates by the American chemist, Dr Hillebrand, he will notice the precautions taken and the degree of accuracy obtained, and will come to the conclusion that the apparent accuracy of many published analyses has no real value. The student, then, must not be discouraged when the results of conscientious work do not seem satisfactory. If a higher degree of accuracy is necessary, he must review his methods—carefully criticise them, at the same time availing himself of the work of others in the current chemical and metallurgical literature.

CHAPTER IV.

THE TECHNICAL ANALYSIS (PARTIAL) OF COAL AND COKE.

For technical purposes the following estimations may be required:—

(1) **Moisture, Volatile Matter, Ash,** and **Fixed Carbon; Sulphur,** and **Phosphorus.**
(2) **Carbon** and **Hydrogen** by ultimate organic analysis.
(3) **The calorific** (or heating) **power** of the coal.

Besides the chemical analysis of *cokes*, there are required the "**Crushing resistance,**" "**Porosity,**" and "**Specific Gravity.**" For information concerning these tests, and the more accurate methods of estimating the calorific power, consult Stillman's *Engineering Chemistry* and Poole's *Calorific Power of Fuels.* In the last mentioned work especially, and in Dana's *System of Mineralogy*, the student will find very complete lists of analyses of the many different kinds of coals. The student must remember, when considering the merits of a coal, that besides the chemical, calorific, and other tests, he must consider the price of the coal. A coal inferior somewhat on these tests to a good steam coal may be recommended, if otherwise favourable, in preference to the good coal, provided the difference of prices on delivery more than counterbalances these deficiencies.

The Analysis of Coal.

Sample the coal, and obtain a 20 gm. sample which has passed through a 100 mesh sieve. From this, carefully sample a few grams, and further reduce in the agate mortar.

(*a*) **Moisture.**—Weigh out two gms. of this sample. Transfer to a weighed 25 c.c. platinum crucible. Place in the air bath, regulated at 105° C., for thirty minutes. Cool in a desiccator and weigh. The loss in weight represents moisture. On further heating it will be found that this loss increases, but any pyrites present is apt to oxidise; therefore it is preferable, when examining coals, to treat all alike for thirty minutes, and consider the result as moisture. The result, though probably inaccurate, is yet sufficient in that it gives a relative idea of the value of various coals.

(*b*) **Volatile Matter** (mostly combustible).—The crucible with lid and contents from (*a*) are now placed over a good single bunsen and cautiously heated to redness for three minutes, then over the blast (gas blowpipe) for other three minutes. Cool in a desiccator and weigh. The loss caused by this ignition is the volatile (mostly combustible) matter, plus one-half of the total sulphur present.

(*c*) **Fixed Carbon.**—The crucible and contents from (*b*) are now placed over the bunsen, the lid being removed. Gentle ignition is continued (assisted by a slow current of oxygen if combustion be very slow) until it is seen that all carbona-

ceous particles have been consumed. The loss in weight caused by this ignition represents the fixed carbon.

(*d*) **Ash.**—The residue left in the crucible is the ash. The difference in weight between 'crucible + lid' and crucible + lid + residue = ash.

Note.—The student must rigidly adhere to the times of ignition given above. The results so obtained, though only relative, serve for the comparison of various solid fuels as regards these constituents.

(*e*) **Sulphur.**—Finely powder in the agate mortar another sample of about 2 gm. coal. From this weigh out 1 gm. Thoroughly mix in a wedgwood mortar with 8 gms. anhydrous Na_2CO_3 and 5 gms. KNO_3. Transfer about one-tenth of the mixture to a large platinum crucible (40 c.c.). Heat to redness, and when combustion is complete add more of the mixture, and continue till all the charge is in the crucible. (If a small crucible is used, either use half the quantities or perform the operation in two stages.) Continue heating for a further fifteen minutes to make sure of completely oxidising the carbon. Cool and transfer to a 300 c.c. beaker, adding about 150 c.cs. water, and gently warm till the mass dissolves. Remove the crucible on a glass rod, washing it down with hot water, keeping it above the beaker. When the outside is washed, grasp the crucible in the fingers and wash out the inside. Filter and wash. Neutralise the solution with HCl. Add an excess of 2 c.cs. 16E. HCl. Boil, and add excess of $BaCl_2$ solution. Let stand in a warm place for twelve hours. Filter, preferably through a "Gooch"; wash well; dry, ignite, and weigh as usual.

The weight of $BaSO_4$ multiplied by 0·1374 gives the weight of S present in the ore taken, 1 gram. From this the percentage is easily calculated.

One-half of this amount has to be deducted from the volatile matter and one-half from the fixed carbon, as in the previous estimations the sulphur was included in these two items.

(*f*) **Phosphorus.**—As in the ash of the coal there may be less than 1 per cent. of phosphoric acid, it is evident that to obtain an accurate estimation at least ·5 gm. ash must be taken for analysis. To obtain this quantity, finely grind 5 or 6 grams of the sample and weigh out 5 gms. Transfer to a wide shallow platinum basin (a piece of foil carefully turned up at the edges, and about 5 cms. square, will do). Place on a platinum triangle, and heat very carefully at a dull red till most of the volatile matter has disappeared. Raise the temperature and continue the combustion at a bright red till the carbonaceous matter has disappeared. The ash is now ready for analysis by any of the known methods.

To bring it into a soluble form, mix the residue with 1 gm. KNO_3 and 4 gms. Na_2CO_3. Fuse till perfectly fluid in a platinum crucible. Dissolve the mass in 50 c.cs. dilute HCl (E.) in a deep beaker. Evaporate almost to dryness, adding towards the end of the evaporation 10 c.cs. HNO_3 (16E.). When almost dry, take up with 6 c.cs. HNO_3 (16E.) and 4 c.cs. H_2O. Filter through a Gooch crucible. Wash well, bringing the bulk of liquid up to about 50 c.cs. Add 30 c.cs. of ammonium molybdate reagent. Let stand for three hours at 40° C., stirring now and then. Filter and wash with HNO_3 (E.) till free from iron, then with water till free from acid. Check the filtrate to see if precipitation was complete. If a Gooch crucible was used, the precipitate may be dried at 100° C. and weighed. The weight thus found multiplied by ·0373 gives the P_2O_5 present, or by ·0179 gives the P present.

(*g*) **The Calorific or Heating Power of Coal.**—Of the many methods used in this determination, the following are a few :—

(1) **Reduction of Litharge** (easy, but inaccurate).

(2) By **calculation** from the **Carbon** and **Hydrogen** contents present (laborious, but where volatile matter is less than 20 per cent. fairly accurate).

(3) By **combustion in a calorimeter** such as a Thomson, Mahler, or other apparatus. Thomson's gives approximate results relatively accurate. Mahler's bomb is to be recommended for both accuracy and simplicity.

Of these various methods the first two will be considered here. Mahler's or Thomson's methods will be found described in Poole's *Calorific Power of Fuels*, or Stillman's *Engineering Chemistry*.

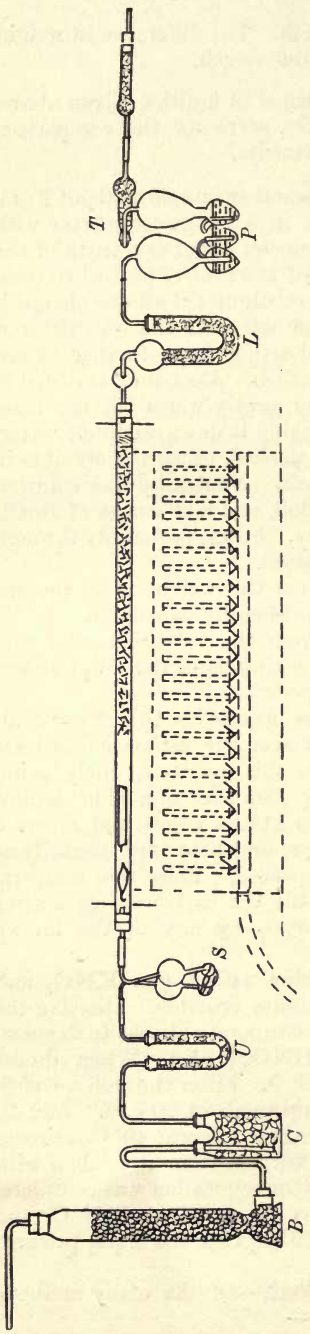

FIG. 103.

(1) By Reduction of Litharge.

Finely powder a sample of the coal in an agate mortar. Weigh out 1 gm. of the powdered coal. Thoroughly mix with 30 gms. litharge by grinding in a wedgwood crucible. Transfer to an E crucible (Battersea round). Clean out the mortar with 20 gm. litharge, and add as a cover on top of the charge. Fire at a bright red heat (using a lid) for 20 minutes. Remove, cool, break, collect and weigh the lead. Run a duplicate.

Theoretically, $2PbO + C = 2Pb + CO_2$, or 12 parts by weight of carbon, reduce 410 parts of lead, or 1 part by weight of carbon reduces 34 parts by weight of lead.

Assume that 1000 gms. pure carbon = 8140 calories (consult a text-book on Heat), then one part of lead represents $\frac{8140}{34} = 239$ calories.

Then if the button from the coal weigh 30·2 gms. the heating value of the coal is $239 \times 30{\cdot}2 = 7217{\cdot}8$ calories per 'kilo' (1000 gms.). In this manner the heating value of coals relative to that of pure carbon is approximately ascertained.

Note.—This is really a determination of the reducing power of the coal, not the heating power. The results are only approximate.

(2) By Calculation from the Carbon and Hydrogen contents,

as determined by ultimate Organic Analysis.

This method will serve both as a check on the previous one and as an exercise in ultimate organic analysis. By

'ultimate' is meant the determination of the percentages of the several elements in contrast to 'proximate' analysis, in which the percentages of combinations of elements such as CH_4 are estimated.

Before proceeding to the analysis the apparatus must be fitted up. Some care is here necessary, but a little time and care in thoroughly fitting and connecting each part will save subsequent vexatious delay.

Taken in order, the necessary apparatus is as follows:—**Oxygen holder**; apparatus for the **purification of the oxygen**; the **combustion tube**; the **combustion furnace**; the **calcium chloride tube** for the absorption of water and the **potash bulbs** for the absorption of carbon dioxide.

The arrangement of the apparatus is shown in fig. 103.

The oxygen may be stored in a cylinder, gas bag, or other suitable apparatus capable of delivering it under slight pressure.

The purification apparatus consists of a cylinder B filled with pumice moistened with strong H_2SO_4. This bottle is connected to the drying bottle C, filled with small lumps of solid **KHO**. Between this bottle and the combustion tube are inserted a U tube (U) filled with soda-lime and a set of "potash bulbs" (S) filled with strong H_2SO_4.

The combustion tube is a piece of hard Bohemian glass tubing, about 75 cm. long and 2 cm. diameter, open at both ends. This tube is filled and fitted as in fig. 104.

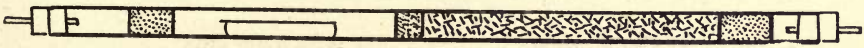

FIG. 104.

c, granular copper oxide; *a*, plug of asbestos; *p*, a porcelain or platinum boat. The end connections are made with good, tight-fitting corks, screens, and tubing, as shown.

The combustion furnace consists of a row of bunsens, each with a tap. The top of the furnace is adapted to accommodate the tube.

The calcium chloride tube L is almost filled with dry granular calcium chloride, in pieces about the size of a *small* pea or grain of wheat. A small plug of cotton-wool is placed on top of the chloride, and then the tube is stoppered either by a sealed cork and leading tube or by ground glass stopper and tube. The tube is connected up as shown.

The "potash bulbs" may be the Liebig, as shown in the purification apparatus, or the Geissler as shown at P. The bulbs are charged about one-third full of a 30% solution of **KHO**, which is introduced by *gentle* suction. The projecting tube T is filled with small lumps of solid **KHO**.

When not in use, the ends of all these drying and absorption tubes are closed with small pieces of rubber tubing and short lengths of glass rod.

Since in the analysis carbon and hydrogen are oxidised to carbon dioxide and water, it is necessary before commencing the analysis to completely remove from the combustion tube all traces of such substances. To do this, disconnect the chloride tubes and potash bulbs. Gently heat the glass tube along its entire length; bring the temperature up to a *low* red. Continue at this temperature for 20 minutes, keeping a slow stream of oxygen passing through the tube.

Weigh the $CaCl_2$ tube and **KHO** bulbs, removing the rubber caps before weighing. This weighing can be done whilst the former operation is proceeding.

Connect the tubes and bulbs, and continue passing oxygen at the rate of

about two bubbles per second for 15 minutes. Disconnect the tubes and bulbs, and reweigh. If there is a gain of more than 2 or 3 milligrams, continue the operation till constant within this limit, taking care that moisture does not condense on the outside of the glass in cold weather. Test the whole apparatus for leaks, by connecting a small tube bent at right angles to the inlet of the drying cylinder on the left. Allow the end of this tube to dip in a little water in a beaker. Apply suction to the outer end of the potash bulbs till the water rises a few inches in the bent tube. Then clamp the rubber on the end of the potash bulbs. If tight, the water level in the bent tube will not drop perceptibly within half an hour. If otherwise, locate the leak by testing each section.

Check the weight of the tubes and bulbs. Transfer 0·5 gm. of the finely powdered coal, dried for half an hour at 103° C., to a weighed porcelain boat, and place in the tube as shown. See that all connections are right. Turn on a very slow stream of oxygen. *Gradually* heat up the part of the tube containing the copper oxide, advancing towards the boat till all the oxide is at a dull red heat, and finally the entire tube from *a* to *d* attains that temperature.

When the coal is completely oxidised (all black particles have disappeared) gradually turn off the bunsens and reduce the temperature, passing a slow stream of oxygen meanwhile. Remove the tubes and bulbs, and weigh. The following example shows how the results are entered:—

1. $CaCl_2$ tube	= 34·3206 gms.	
,, ,,	+ H_2O = 34·4296 ,,	
	H_2O = 0·1090 ,,	
2. KHO bulbs and tube	= 32·8104 gms.	
,, ,, ,,	+ CO_2 = 34·4464 ,,	
	CO_2 = 1·6360 ,,	
3. Porcelain boat	= 6·3212 gms.	
,, ,,	+ Ash = 6·3425 ,,	
	Ash = 0·0213 ,,	

The results now are—

H_2O = 0·1090 gm. = ·0121 gm. H,	= 2·42%	H
CO_2 = 1·6360 ,, = ·4461 ,, C	= 89·22%	C
Ash = 0·0213 ,, =	4·26%	Ash
Sulphur (already determined)	= 0·32%	S
Nitrogen (not determined, but assumed)	= 0·50%	N
Oxygen, by difference,	3·28%	O
Total,	100·00%	

The nitrogen estimation (by combustion or by Kjeldahl's process) is omitted, but in the example has been assumed, in order to show the complete calculation. Now, as this analysis has been carried out on *dried* coal, moisture is not included. Assume that this moisture was found to be 2%, then when this item is inserted we have—

Moisture,	2·00%
Hydrogen,	2·39%
Carbon,	87 47%
Sulphur,	0·31%
Nitrogen,	0·49%
Ash,	4·17%
Oxygen,	3·20%

The calorific power is now ascertained as follows:—

Assume that the unit of heat "*one calorie*" is the quantity of heat required to raise the temperature of one kilo (1000 gm.) water 1° C.

The following data have been obtained by experiment:—

1 kilo *carbon* burning to CO_2	produces	8,140	calories
1 „ *sulphur* „ „ SO_2	„	2,220	„
1 „ *hydrogen* „ „ H_2O (condensed)	„	34,500	„
1 „ „ „ „ „ (steam at 100 C.)	„	28,901	„

Then, if **C**, **H**, **O** and **S** represent the percentages of carbon, hydrogen, oxygen and sulphur respectively the calorific power

$$= \frac{8140\mathbf{C} + 34500\left(\mathbf{H} - \frac{\mathbf{O}}{8}\right) + 2220\mathbf{S}}{100}$$

$$= \frac{(8140 \times 87{\cdot}47) + 34500(2{\cdot}39 - 0{\cdot}40) + (2220 \times 0{\cdot}31)}{100}$$

$$= \frac{781349}{100} = 7813{\cdot}49 \text{ calories}$$

The student will note that in this formula there is deducted from the %**H** an amount sufficient to combine with all the **O** present to form H_2O. As **H** and **O** so united in the coal are of no value for heating purposes, this quantity of **H** is accordingly deducted as shown.

Now, in practice, when **H** burns, a considerable amount of the products of combustion escape as steam and are not condensed, and in this state a certain amount of the heat becomes latent, and for heating purposes is not available. Also, whatever moisture is in the coal has to be heated up to boiling point, and converted into steam at the expense of the carbon and hydrogen in the coal. The heat so consumed is again not available in practice; hence the following modification of the formula gives more accurate results:—

$$\text{Calorific power} = \frac{8140\mathbf{C} + 28901\left(\mathbf{H} - \frac{\mathbf{O}}{8}\right) + 2220\mathbf{S} - 622\,\mathbf{W}}{100}$$

(Where **W** = % moisture and 622 = calories necessary to change 1 kilo water at 15° C. into steam at 100° C.).

$$\text{Calorific power} = \frac{(8140 \times 87{\cdot}47) + (28901 \times 1{\cdot}99) + (2220 \times 0{\cdot}31) - (622 \times 2{\cdot}00)}{100}$$

$$= 7639{\cdot}61 \text{ calories}$$

The Analysis of Cokes.—The student need not, unless he have ample time, proceed with a detailed analysis of coke. A good coke should be low in ash,

sulphur, and phosphorus, and high in fixed carbon. It also should be up to a certain physical standard as regards crushing resistance, porosity, specific gravity, etc. (consult *Coke: its Manufacture and Recovery of Bye-Products*, by John Fulton). The same authority quotes the following as a chemical standard for good coke :—

Fixed Carbon,	87·46%
Ash,	11·32%
Sulphur,	0·69%
Phosphorus,	0·029%
Moisture,	0·49%
Volatile matter,	0·011%

The methods of estimating these substances have been given, and need not be repeated. In many cases the analysis may be cut down to "fixed carbon," "sulphur," and "phosphorus." In technical work complete analyses are not, as a rule, required, and only a few, or in some cases only one substance requires estimation. The chemist in such cases modifies the complete scheme accordingly.

CHAPTER V.

THE TECHNICAL ANALYSIS OF FIRECLAYS AND CEMENTS.

In considering the value of a cement or fireclay, it must be remembered that the mere chemical composition is by no means the sole guiding point. In the case of a cement the degree of fineness, tensile strength, and other points also require determination; therefore the necessary tests may be subdivided into two classes — chemical and mechanical. The purely mechanical tests lie entirely outside of the scope of this work, but on account of their importance, and to prevent the student falling into the mistake of supposing that his chemical analysis yields all the necessary information, a very brief account of the necessary mechanical tests is given.

The Chemical Examination of Cements.

A suitable material for the student to operate on is the well known brand —Portland Cement. As the student has already examined in detail a silicate, the following notes are given somewhat briefly. A good cement should consist chiefly of SiO_2 and CaO, with a little Al_2O_3 and Fe_2O_3, and less than 2% MgO, and 1·5% CO_2 and SO_3. From this the student will see that the accurate determination of MgO, CO_2, and SO_3 is a matter of much importance, and that in many cases the determination of these three items may be sufficient to decide the fate of the cement. The student, however, is advised to work out the complete scheme, as a check is thus obtained on the accuracy of his work.

SiO_2.—Take 1·5 gms. finely powdered cement and boil in a porcelain evaporating basin with 50 c.cs. aqua regia. Evaporate to dryness. Add 100 c.cs. HCl (5E.). Boil and filter into a 500 c.c. flask. Wash well, allowing washings to come up to the mark. Reserve the solution, which contains Fe_2O_3, Al_2O_3, CaO, MgO, K_2O, Na_2O, SO_3.

Dry the residue, and fuse with five times its weight of a mixture of K_2CO_3 and Na_2CO_3 in a platinum crucible. Cool, dissolve, and treat as before described for SiO_2. Reserve the solution, which contains some Al_2O_3.

Al_2O_3,Fe_2O_3.—Precipitate the Al_2O_3 in this last solution by means of NH_4HO. Filter, wash, dry, ignite, and weigh.

Agitate the solution in the 500 c.c. flask. Transfer 300 c.cs. to a beaker. Render alkaline with NH_4HO. Boil, filter, and wash. Redissolve and repeat precipitation. Reserve the filtrates. The precipitate consists of $Al_2(HO)_6$ and $Fe_2(HO)_6$. Separate and estimate the Fe_2O_3 and Al_2O_3 as before. Calculate back from 300 c.cs. to 500 c.cs. Add the Al_2O_3 to that obtained in the filtrate from the SiO_2, and the total Al_2O_3 and the Fe_2O_3 are thus obtained.

CaO.—To the filtrate from the iron and the alumina add $(NH_4)_2C_2O_4$ in slight excess. Allow to stand for a few hours. Filter and wash with dilute

NH_4HO (E.). Redissolve and repeat precipitation. Reserve the filtrates. Estimate the CaO in the CaC_2O_4 (precipitate) volumetrically by means of a standard solution of $K_2Mn_2O_8$ (checked on a pure lime salt).

MgO.—The filtrate from the lime, if of large bulk, is evaporated to about 100 c.cs. in a porcelain evaporating basin, and is then transferred to a platinum dish and evaporated to dryness, and then ignited to expel all ammonia salts. Cool, add 50 c.cs. water and boil for five minutes. This dissolves out the alkalies (generally as sulphates) and any $MgSO_4$ that may be present, and leaves as a residue MgO. Filter, wash, dry, ignite, and weigh the MgO. Reserve the filtrate, which is now, after the addition of 3 or 4 drops of strong H_2SO_4, evaporated to dryness and ignited till constant, the weight representing $MgSO_4 + K_2SO_4 + Na_2SO_4$. Dissolve in 50 c.cs. water. Carefully divide the solution into two equal parts. In one add a little HCl (5E.), make alkaline with NH_4OH, and estimate the MgO as usual with Na_2HPO_4. Calculate the MgO found here and before, back to the 500 c.cs. taken (multiply by $\frac{5}{3}$ in the first case and $\frac{5}{1{\cdot}5}$ in the second). The result is the total MgO.

K_2O, Na_2O.—To the second portion of the solution containing $MgSO_4$, K_2SO_4, Na_2SO_4 add a solution of $PtCl_4$ in slight excess. Carefully evaporate to dryness on the water bath. Take up, as before, with alcohol, and filter off the K_2PtCl_6, weigh and convert to K_2SO_4. Add the $MgSO_4$ previously found, and subtract the $K_2SO_4 + MgSO_4$ from the $K_2SO_4 + Na_2SO_4 + MgSO_4$ previously found, and the result is Na_2SO_4. Convert the K_2SO_4 and Na_2SO_4 to K_2O and Na_2O. Take care that in these calculations account is taken of the amount of solution; that is, the fraction of the total solution employed for each estimation. Out of 500 c.cs., 300 c.cs. were taken, and this quantity was again subdivided into two lots of 150 c.cs. each. The $MgSO_4$, K_2SO_4, Na_2SO_4 was estimated in 300 c.cs., the K_2SO_4 in 150 c.cs. Multiply this by 2 and subtract, and the result is $MgSO_4$,Na_2SO_4 in 300 c.cs. The $MgSO_4$ was determined in 150 c.cs. Multiply by 2 and subtract, and the result is Na_2SO_4 in 300 c.cs. This multiplied by $\frac{5}{3}$ gives the Na_2SO_4 in the 500 c.cs. (corresponding to 1·5 gms.) The student must in a similar manner estimate the K_2SO_4, and then convert the results to Na_2O and K_2O.

SO_3.—The remaining 200 c.cs. of solution are now examined for SO_3 by precipitation with barium chloride; the SO_3 is calculated in the $BaSO_4$ found, and then calculated back to the 500 c.cs., the percentage then being worked out on the 1·5 gm. taken for analysis.

CO_2.—As only small quantities of this compound are, as a rule, present, it is necessary to take from 5 to 10 grams for analysis. The analysis is conducted as before described, and may be omitted at present.

The following table gives the limits within which the constituents of good "Portland" cements vary.

CaO, . .	58% to 67%
SiO_2, . .	20% „ 26%
Al_2O_3, . .	5% „ 10%
Fe_2O_3, . .	2% „ 6%
MgO, . .	0·5% „ 3%
K_2O / Na_2O . .	·5% „ 2%
SO_3, . .	0·5% „ 1·5%
CO_2, . .	0·5% „ 1·5%

From this it will be seen that after manufacture the cement consists chiefly of silicate of lime.

Mechanical Tests.

(*a*) **Fineness.**—Samples of the cement are sifted, and that which passes through a 100 mesh sieve is taken for analysis. The proportion remaining on the sieve is estimated. The finer the cement the higher its value.

(*b*) **Resistance to Cracking.**—Small cakes of cement are made of stiff consistency, and the time of setting to withstand a wire-cutting test is noted. The cakes when dry are examined for cracks, and compared with specimens from cements known by experience to be of good quality.

Tensile Strength.—Cement, sand, and water are carefully mixed in definite proportions, and pressed into moulds under uniform conditions. The briquettes are further treated, and then tested in a suitable testing machine (the Riehlé or other), and the results compared with certain standards set up for good cements.

THE ANALYSIS AND EXAMINATION OF FIRECLAYS.

For practice the student may take either "Stourbridge" or "Dinas" fireclay and sand. The following table gives their average composition. The Dinas sand consists almost entirely of SiO_2 (free), but in the Stourbridge clay the SiO_2 is mostly combined with Al_2O_3. The clay is preferable for practice.

	Stourbridge.	Dinas.
SiO_2 (free),	...	98·31
„ (combined),	64·92	
Al_2O_3,	23·53	0·72
Fe_2O_3,	2·14	0·18
H_2O,	6·91	0·35
CaO,	0·33	0·22
MgO,		
K_2O | Na_2O	0·50	0·14
Moisture,	1·80	
TiO_2,		
SO_3,		
Organic Matter,		

For reference regarding the composition of clays, the student may consult *Tables of Analyses of Clays, etc.*, by Alfred Crossley. He will there find tabulated lists of analysis of all the most important fire and other clays, sands, etc.

The Chemical Analysis.—The analysis of fireclays much resembles that of silicates (previously given). For the present the student need only estimate SiO_2 (free, combined, and hydrated), Al_2O_3, Fe_2O_3, and H_2O. Then if, on summing up results, there remains unestimated more than 3%, he must proceed further with the analysis.

SiO_2 (free, combined, and hydrated).—Estimate the total SiO_2 by fusing 1 gm. clay (dried at 100° C.) with Na_2CO_3,K_2CO_3. Fuse for twenty to thirty minutes. Cool and treat as before directed (see Analysis of Silicates). The result is the *total* SiO_2.

Free SiO_2.—Take 1 gram clay dried at 100° C. and digest with H_2SO_4 (20E.) for about eight hours. Evaporate to dryness. Cool. Take up with water. Filter. Wash well. The residue consists of free + combined + hydrated silica + bases (if any). Transfer in small portions to a boiling solution of

Na_2CO_3 (5E.), filtering now and then so as to replace the Na_2CO_3. When all the solution has been transferred to the platinum crucible containing the Na_2CO_3, continue the boiling, replacing the Na_2CO_3 till no reaction is obtained with NH_4Cl (see Qualitative Analysis). This treatment dissolves out combined and hydrated SiO_2 and leaves free SiO_2. Dry, ignite, and weigh.

Hydrated SiO_2.—Treat 5 gms. dried clay with boiling Na_2CO_3, omitting the H_2SO_4 digestion. Boil repeatedly. This dissolves out hydrated silica. Filter, add HCl and evaporate to dryness, and estimate the SiO_2, which is reported as hydrated silica.

Combined SiO_2.—Subtract free + hydrate SiO_2 from the total 'residue' free + combined + hydrated SiO_2 + bases. The result is *combined* SiO_2 + *bases*. If the 'total residue' is greater than the 'total SiO_2' previously found, the difference represents the bases along with the combined SiO_2.

Water of Hydration.—Take 1 gram of clay dried at 100° C. and ignite at a red heat in a platinum crucible over the blowpipe till constant. The loss represents combined water. Al_2O_3, Fe_2O_3, **Alkalies**, etc. are determined as usual.

The student will find, on consulting works of reference, that a good fire-clay should not contain more than 2% Fe_2O_3 and 1% of K_2O or Na_2O. That the importance of fixing such limits may be brought home to the student, the following 'fire-tests' should be performed :—

Tests concerning the fusibility of Fireclay.—Pass a sample of the dry clay through a 30 sieve. Mix one-third of the sample with a little water. Dry slowly. Place in a crucible in the wind furnace and burn at a good red heat. Cool. Crush and pass through the 30 sieve. Now mix one part of the burnt clay with two parts of the unburnt; add a little water, kneading well. Allow the kneaded mass to stand over-night. In the morning cut out with a sharp knife small test pieces like a T with the leg 1 cm. long and the cross piece about 2·5 cms. in length; width of face about ·3 cm.; depth about 1·2 cm. Also cut small pyramids, square base, and about 2·5 cms. high. Gently dry these pieces. Lute two E crucibles to a half brick (by means of clay). Set the half brick and crucibles on the fire bars. Insert the test pieces and lute on the lids, build up the fire. Fire at a red heat and raise the heat to a whiteness, continuing as closely as possible at this temperature for about two hours, using anthracite or the hardest coke for firing. Remove, cool, break crucibles, and examine the test pieces along the edges with a powerful lens. The edges should be sharp and unglazed. Take now three lots of the clay. To one lot add 5% Na_2CO_3, to the second add 5% Fe_2O_3, and to the third add 5% CaO. Prepare test pieces. Treat as before, and note the results.

Tests concerning resistance to Corrosion.—An absolute standard cannot be laid down, but a useful comparison may be obtained by testing the clay against some well known brand such as the "Battersea." With the mixture of burnt and unburnt clay, mould small scorifiers of approximately the same shape as the Battersea 5 cm. scorifier. Dry carefully, and burn at a good red heat. Place in the scorifiers the following charges: in one 20 gms. PbO, in another 20 gms. granulated copper and 1 gm. borax. Place similar charges in two Battersea scorifiers. Transfer the four charges to a muffle between a red and white heat. (For safety, insert in the muffle a flat tile to catch any metal that may run through.) Continue the fusion till one scorifier is perforated. Remove, pour, and examine for corrosion. Note the results. If time be available, the student may proceed to study the effect of varying proportions of different impurities on corrosion.

CHAPTER VI.

A PARTIAL EXAMINATION OF SHALE OIL, PETROLEUM, AND LUBRICATING OILS.

THE subject here touched upon is one that can only be successfully handled by an expert chemist with a thorough training in both inorganic and organic chemistry; yet, as the metallurgical chemist may be asked to value a shale or petroleum, examine an oil for lubricating purposes or for the preservation of winding ropes—for these and other reasons this section has been inserted. Too frequently the metallurgical student's training in organic chemistry is deficient, but it is hoped that he may be able to follow out the instructions given. That he may understand something of the composition of the materials examined and the reactions involved, he is recommended to peruse Remsen's *Elementary Organic Chemistry*, or, if he intends following the subject further, he should, if possible, take up a systematic course of study—both theoretical and practical—in organic chemistry.

The methods here given are, at the best, somewhat patchy and brief, and suffer from the attempt to condense into a few pages matter which generally taxes the resources of a complete volume. The student therefore is recommended, on completing the tests here given, to consult *Commercial Organic Analysis*, vol. ii. part ii., Allen (and Leffmann); also the technical methods of examining petroleum, lubricating and other oils, as given in Stillman's *Engineering Chemistry*; also *Lubrication and Lubricants*, by Archbutt and Deeley.

The following table given by Allen shows the nature and quantity of the products obtained from typical examples of American petroleum and Scotch shale oil. The student must remember, however, that considerable variations are met with in petroleums and shale oils, and that substances present in one may be absent in another. For instance, 'kerosene' from bituminous shale consists chiefly of ethenes (see Remsen), and from American petroleum largely of methanes.

Products.	From Petroleum.		From Shale Oil.	
	S.G.	Percentage.	S.G.	Percentage.
Cymogene and Rhigolene . .	·590–·625	trace	...	trace
Gasolene	·636–·657	1·0–1·5		
"C" Naphtha (benzin naphtha) .	·700	10·0	·730	5·0
"B" Naphtha	·714–·718	2·5		
"A" Naphtha benzin . . .	·725–·737	2·0–2·5		
Kerosene (burning oil) . . .	·802	50·0–55·0	·800–·810	37·0
Lubricating Oil	·875	17·5	·885	17·0
Paraffin Wax	...	2·0	...	13·0
Coke, gas and loss . . .	...	8·0–10·0	...	28·0

In the following partial examination of shale oil the student will see that the substances just detailed are not estimated singly but in four groups, in the ascending order of specific gravity ·780, ·803, ·867, and residue over ·867. For further separation of these groups consult Allen's *Organic Analysis.*

THE EXAMINATION OF SHALE.

An approximate idea of the nature of a shale may be obtained on examination by the method given for coals, but a more accurate idea of the commercial importance of its contents is obtained by the following method of 'destructive distillation.' (For the market value of shales, petroleum, etc., consult *The Mineral Industry.*)

The following tabulation (simplified and adapted from that given by R. Tervet in Allen's *Analysis*) serves to give the student a bird's-eye view of the various steps in the partial analysis.

The quantities of materials on the left are subject to considerable variation, and are inserted merely as an indication of what may be expected.

1. 3000 gms. **Shale.** Distil at a dull red.
2. 500 c.cs. **Crude Oil.** Distil with steam.
3. 450 c.cs. **Once-run Oil.** Treat with acid. — *Coke.*
4. 400 c.cs. **Acid-washed Oil.** Treat with soda. — *Acid Tar.*
5. 390 c.cs. **Once-purified Oil.** Distil to dryness. — *Soda Tar.*
6. *a* **Naphtha** 2 c.cs. (?) ·780 | *b* **Crude Light Oil** 150 c.cs. ·803 | *c* **Heavy Oil** 210 c.cs. ·867 | *d* **Still Bottoms** 1 or 2 gms.

These products are not pure, but are mixtures. A certain amount of "naphtha" is mixed with the "crude light oil" and the "heavy oil." Again, the greater part of the "heavy oil" consists of "lubricating oils," and of the lesser part the bulk is "paraffin." (See "Allen.")

1. Details of the Analysis.—Take a 3000 gm. sample of the roughly powdered shale (10 sieve). Transfer to a large iron retort. Carefully lute on the lid with a paste of whiting. In a suitable furnace build a fire. Insert the retort and arrange a supply of cooling water for the tube, and connect the mouth of the tube to a large distillation flask. Build the fire up round the retort, enclosing it if necessary with temporary walls of loose bricks. When water begins to drip from the tube, turn on the cooling supply, taking care that none of it finds its way into the flask. A certain amount of gas comes over at first and is lost (unless specially collected). Then water and oily matter follow. Continue the distillation for two or three hours till no more matter comes over. The retort should now be red-hot. Remove the cooling cloth from the tube, and with a large bunsen or other means gradually heat the tube from the neck downwards to expel any matter lodged in the tube. Remove from the fire, and when cool open and weigh the residue as a check on the estimation. The flask now contains the greater portion of the distillate (except gaseous matter).

2. **Distillation of the Crude Oil with Steam.**—Arrange the distillation apparatus as in fig. 105.

The flask on the left generates steam, which passes over into the distillation flask and aids the distillation of compounds boiling far above 100° C., the atmospheric pressure being divided between the water and oil, thus

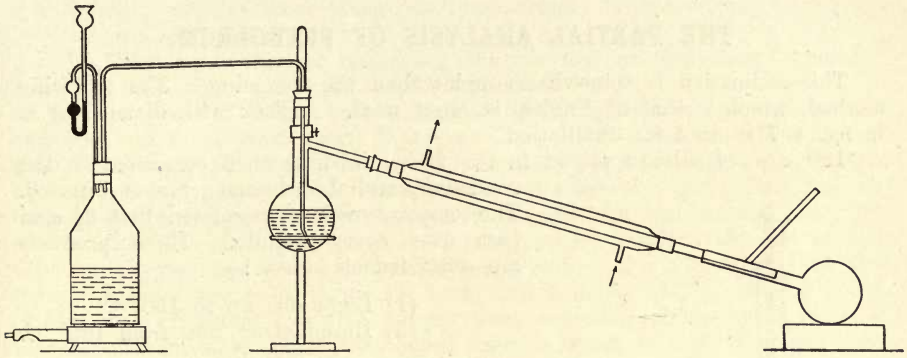

FIG. 105.

reducing the pressure on the oil, and obtaining the same result as by distillation in a partial vacuum. The mercury in the safety funnel acts as a safety valve.

Before proceeding with the distillation, take the specific gravity of the oil, either by the ordinary hydrometer, converting degrees Baumé into the usual reading, and making the necessary corrections for temperature, or if only small quantities of the liquid are available, the Araeopicnometer of Eichhorn is very convenient.

The distillation is now commenced, the steam being first prepared, and then the heat is applied to the oil, through which the steam is slowly passed. Continue the distillation to dryness. The residue in the flask is "coke."

3. **Treatment of the "Once-Run Oil."**—The distillate in the receiver is transferred to a separator (fig. 106), and is warmed to about 40° C. by immersing the separator in warm water. Any water separating is run off. Then add 5% by volume of H_2SO_4 (S.G. 1·70) and agitate for ten minutes, plunging the separator into water at 35° C. to keep down the temperature. Allow to stand in the water for half an hour. Then run off the "acid tar."

FIG. 106.

4. **Treatment of the "Acid-Washed Oil."**—To the contents of the separator add 20 c.cs. **NaHO** (S.G. 1·30). Warm to about 40° C. for half an hour and run off the "soda-tar."

5. **Treatment of the "Once-Purified Oil."**—Measure and take the specific gravity of the contents of the separator. Transfer to a clean distillation flask and proceed with the distillation. When the distillate reaches S.G. ·780 replace the receiver by another. (Test the S.G. with a small Sprengel tube, the "water contents" of which are known. See "Allen.") This first product is termed "**naphtha,**" and is only yielded by some oils. Measure the quantity obtained, if any.

Proceed again with the distillation till a drop of the distillate on a cold spatula shows signs of solidifying. Replace the receiver. The product thus obtained is "**crude light oil.**" Measure and take the S.G. of the quantity thus obtained.

Continue the distillation. If a viscid brown or yellow product appears, stop the distillation. Measure and take the S·G. of the distillate, which is termed "**heavy oil.**" The residue in the flask is termed "**still bottoms.**"

From the volumes and S.G.'s of the products thus obtained, their percentages by weight may be calculated on the original sample of shale.

THE PARTIAL ANALYSIS OF PETROLEUM.

This estimation is somewhat simpler than the foregoing. The following method, which is that of Engler, is often used. A flask with dimensions as in fig. 107 is used for distillation.

100 c.cs. of oil are placed in the flask, which is then connected to the condenser, and the thermometer is inserted. The temperature is so regulated that $2\frac{1}{2}$ c.cs. pass over every minute. Three products are separated as follows:—

(1) Light oils up to 150° C.
(2) Illuminating oils from 150° C. to 300° C.
(3) Residual matter.

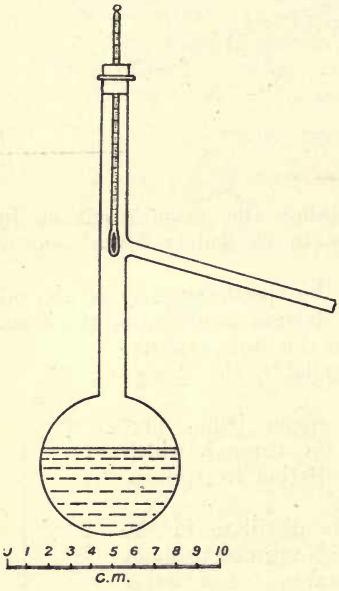

FIG. 107.

Group (1) consists of cymogene, rhigolene, petroleum, ether, gasoline, naphtha, ligroin, and benzin.

Group (2) consists of varieties of kerosene.

Group (3) consists of lubricating oils, paraffin oils, and coke.

(For further details consult "Allen" and "Stillman.")

A PARTIAL EXAMINATION OF LUBRICATING OILS.

The complete examination of lubricating oils involves much work and outlay for special apparatus. The following brief notes are given to enable the student to determine the acidity of an oil, its liability to oxidation, and other points which are of vital importance when an oil is used for fine machinery, or for the preservation of winding ropes (steel). In this latter case the lives of men often depend on the preservation of a rope, and it may be that a particular oil is used to protect it from acid waters, and that the oil itself may be as corrosive as the water. A low grade mineral oil may contain sulphuric acid which has been used for its purification, and has not been afterwards completely removed. Or again, an oil may contain organic acid, or, though not at the outset containing free acid, it may be so decomposed under certain circumstances that free acids are produced. The following points will therefore be considered here:—

(1) **The Oxidisability of an Oil.**
(2) **The Acidity of an Oil.**
  (*a*) *As obtained from the manufacturer.*
  (*b*) *After subjection to a high temperature in contact with water.*

For determinations of viscosity, solidification, flash point, coefficient of friction, etc., consult the authorities previously mentioned.

(1) **The Oxidisability of an Oil.**—Most mineral oils and land animal oils are practically free from drying tendencies. Fish oils (except "sperm" and "bottlenose" oil) are less perfect in this respect. The vegetable oils differ considerably, some of them being far from perfect. This tendency to dry up is often termed 'gumming.'

The following method of estimating the 'drying' or 'gumming" qualities of oils is that of Fresenius, as modified by Bach.

Take a piece of 2 cm. bore soft glass tubing, closed at one end, and of sufficient length to hold about 200 c.cs. Draw it out to about 1 cm. bore near the other end. By means of an accurate pipette transfer 1 gm. of the oil to the tube. (Mark the pipette so that it delivers 1 gm. This may be done by delivering into a counterpoised watch glass on the balance pan. By a few trials the right point will soon be found.) Displace the air in the tube by oxygen, and seal up by the foot blowpipe the narrow part of the tube. Transfer the tube to an air bath, and heat at 110° C. for 10 hours (taking due precautions against danger from explosion of the tube). Allow to cool. In a beaker place 200 c.cs. of water. Break off the tip of the tube under the water, which then, if the oil has been oxidised, will enter the tube. Remove the tube with the water absorbed. Measure the residue in the beaker. The difference between this and 200 c.cs. represents the volume of oxygen absorbed. At the end of the experiment, test with a glowing splinter for free oxygen, and if none is present repeat the test with a larger tube or a smaller quantity of oil.

Mineral oils, as a rule, absorb very little oxygen; vegetable oils such as "rape," "olive," "cottonseed," large quantities (for further data see "Allen").

(2) **The Acidity of an Oil.**

(*a*) *As obtained from the manufacturer.*

Mineral Acids (generally H_2SO_4) may be present as an accidental impurity. To test for such impurity, boil the oil with water for about 15 minutes. Separate the aqueous liquid. In one quarter of this liquid test for acid with methyl orange solution. A red colour indicates mineral acid. In another quarter test for the various acids with $AgNO_3$, $BaCl_2$, etc. In the remaining half estimate by the usual methods the acid found, if any.

Free Fatty Acids.—Warm 50 c.cs. alcohol (rect. spirit) to about 40° C., and add 10 drops of an alcoholic solution of phenolphthalein, and from a burette gradually add standard KHO (35 c.cs. = 5 c.cs. N. H_2SO_4) till a pink tint is obtained. Add 20 gms. of the oil to the solution. Keep the temperature about 40° C., and agitate for about five minutes. If acid is present the pink disappears. Now gradually add from a burette more KHO, till on agitation a permanent pink is obtained. The number of c.cs. of KHO taken in this last operation divided by 4 give the percentage of free fatty acid. If free mineral acid has previously been found, it either must be allowed for or previously removed by repeated agitation with water.

(*b*) *After subjection to a high temperature in contact with water (steam).*

This determination is of importance, as oils are frequently used in contact with superheated steam, and under such conditions 'fatty oils' are more or less decomposed into free fatty acids and glycerol. Such oils therefore should not be used for cylinders.

Heat 50 gms. oil + 50 gms. water in a strong bottle, with the stopper tied down, the bottle being immersed in boiling water. Agitate every now and then (taking precautions against explosion). After about 6 hours remove, and separate the aqueous liquid from the oil.

(α) *The aqueous liquid.*—Estimate the H_2SO_4 present. Any increase on that previously found is due to the decomposition of sulphonates (see Remsen), and if the increase be considerable, indicates an objectionable oil.

(β) *The oil.*—Titrate as before with KHO and phenolphthalein in an alcoholic solution. Any increase on the fatty acids previously found indicates decomposition of 'fatty oils.'

Note.—In the case of cylinder oils for high-pressure cylinders, immerse the bottle in $CaCl_2$ solution at 150° C. For general purposes, however, a temperature of 100° C. suffices to condemn or pass an oil.

CHAPTER VII.

THE PARTIAL ANALYSIS OF IRON AND STEEL.

Such matter is presented in this chapter as will give the student some insight into the methods of analysis used in the technical examination of iron and steel. The nature of this work prevents a detailed treatment of the subject—a treatment which may demand an estimation of any one or more of the following substances:—*Carbon* (free and combined), *sulphur*, *silicon*, *phosphorus*, *manganese*, *titanium*, *copper*, *nickel*, *cobalt*, *chromium*, *aluminium*, *arsenic*, *antimony*, *tin*, *tungsten*, *vanadium*, *nitrogen*, *iron*. Generally, the estimations most required are those of **carbon**, **sulphur**, **silicon**, and **phosphorus**. Of the other elements and compounds mentioned, determinations of one or more are required in the case of special steels. For information regarding these determinations the student is referred to *Chemical Analysis and Foundry Chemistry*, by Crobaugh; *The Chemical Analysis of Iron*, by Blair; "Carbon in Steel by Direct Combustion," by Blount, in *The Analyst*, Jan. 1902; "Sulphur in Wrought Iron and Steel," by Auchy, in the *Jour. Amer. Chem. Soc.*, March 1901, and other articles in the same journals. The student who wishes to go further should, if possible, obtain access to the papers and articles of Campbell, Drown, and others, published from time to time in the various chemical and metallurgical journals.

As the student's time is limited, he may for the present postpone the estimation of silicon and phosphorus, though these are given on account of their importance both to the metallurgist and the foundryman.

In order that the student may obtain a more thorough grasp of the subject, a few notes on the composition and properties of the substances considered will not be out of place. Regarding the influence of the various elements on steel, consult *The Manufacture and Properties of Structural Steel*, by H. H. Campbell.

Carbon exists in iron in three states—*graphitic*, *dissolved*, and *combined*. Besides these, other forms have been identified by the microscope.

Sulphur exists in iron chiefly as the *sulphide* **FeS**, which is soluble in molten iron.

Phosphorus exists as *phosphide of iron*, which is completely soluble in the molten iron.

Silicon forms *silicide of iron*, which also is soluble in molten iron.

Of these four elements, then, carbon is the only one which can exist in the free state. The variations in the proportions of the various elements present are almost infinite, but the following brief tabulation gives the approximate composition of pig-iron, wrought iron, and steel, though each of these is subject to considerable variation.

	Pig-Iron.	Wrought Iron.	Steel.
Graphite . . .	2·650	—	—
Combined Carbon .	0·462	0·07	0·360
Sulphur . . .	0·064	0·04	0·042
Silicon . . .	2·120	0·14	0·061
Phosphorus . .	0·040	0·08	0·056
Manganese . .	0·122	0·14	0·620
Iron (by difference) .	94·542	99·53	98·861

The student is required to estimate the following:—

(1) **Carbon.** (*a*) *Total.*
(*b*) *Graphitic.*
(*c*) *Combined.*
(2) **Sulphur.**
(3) **Silicon.** (If time permits.)
(4) **Phosphorus.** (If time permits.)

(1) CARBON. (*a*) Total

In this estimation the carbon is converted into CO_2 which is absorbed in caustic potash. From the weight of CO_2 thus obtained the carbon is calculated.

At first sight it would appear that the simplest procedure would be to ignite the iron or steel borings directly in a current of oxygen and absorb the CO_2 thus formed in KHO. Unfortunately this method, so far, has either proved inaccurate, or where complete combustion was obtained, the apparatus necessary to withstand the high temperature or other variations in treatment was not suited to technical work (see articles by Blount in *The Analyst*). The student will find that the method here given is by no means ideal, from a technical standpoint, on the score of convenience and rapidity, and there seems a probability of it being replaced in the near future by some quicker direct oxidation method.

Method adopted.—On reference to the many works on this subject, a large variety of methods will be found. The method here given will with ordinary care give accurate results. Briefly it is as follows:—

The iron is dissolved in a solution of double chloride of potassium and copper, made acid with HCl. Metallic copper is precipitated and redissolved; the iron is dissolved, the carbon being left in suspension. It is then collected and ignited in the combustion furnace with oxygen, and the CO_2 evolved weighed.

Solution of the Iron.—Weigh out 1 gram of pig-iron borings. Transfer to a 300 c.c. beaker. Add 100 c.cs. $CuCl_2,2KCl,2H_2O$ solution, which is made as follows. Dissolve in water 149·1 parts KCl and 170·3 parts crystallised $CuCl_2,2H_2O$. Evaporate and crystallise out the double chloride. Dissolve 300 gms. of the double salt in distilled water. Filter through ignited asbestos, and preserve in glass stoppered bottles.

To the contents of the beaker add 7 c.cs. HCl to render the solution acid. Stir intermittently till solution of the iron is effected. Place the beaker and contents towards the end of the solution on a water bath at a temperature of about 60° C. The following reactions are taking place—$Fe + CuCl_2 = FeCl_2 + Cu$ and $Cu + CuCl_2 = 2CuCl$. The KCl simply aids the solution of the precipitated copper. In about 40 minutes from the addition of the double chlorides, solution should be nearly complete and most of the copper dissolved. Wash down the sides of the beaker with a little acidulated double chloride. To the solution add a little ignited asbestos to settle the carbonaceous matter and prevent it clogging the filter (as recommended by Barba).

For filtration, special platinum boats, fitted on the principle of the Gooch crucible, are very convenient. The student may, however, filter off the carbonaceous matter by means of a Gooch crucible aided by artificial suction, the carbonaceous matter being washed in with a jet of water after the liquid has passed through the filter. Carefully wash the carbon on the filter with hot water. Dry the crucible and contents in the air oven at 100 C. The carbonaceous matter is now ready for ignition.

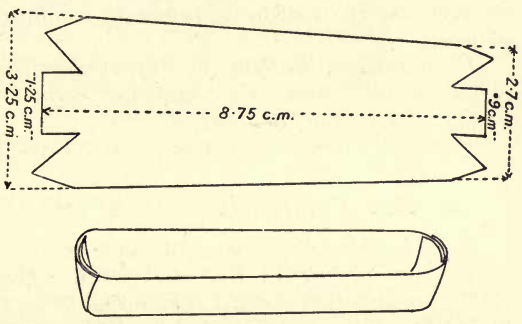

FIG. 108.

Oxidation of the Carbon.—Prepare a platinum boat by cutting a piece of platinum foil as in fig. 108, folding up the sides and ends to form a trough. Transfer the carbonaceous matter and asbestos from the Gooch to the boat.

The combustion furnace, accessories and fittings must be set in order. The oxygen purification apparatus is again used, but this time is provided with a three-way tube, with taps inserted between the storage and the purifiers. This permits a current of air being drawn through the apparatus. The combustion tube may be of hard Jena glass, porcelain, or platinum. Two U tubes are used between the furnace and the potash bulbs. The limb of the first tube nearest the furnace contains anhydrous $CuSO_4$, the other limb anhydrous CuCl. The second U tube contains *dried* $CaCl_2$. These two tubes form the 'purifying train.' The CuCl absorbs any Cl, and the other substances any H_2O. This set will serve for many determinations. The potash bulbs and guard tubes follow, and an aspirator should be handy to draw a current of air through the apparatus when required. The potash bulbs are charged with 8E. KHO, and the guard tube with $CaCl_2$. Test the furnace and bulbs as before described (see Coal and Coke), the tube being charged as in sketch, the boat being for the present kept in the air oven at 100° C.

When all is ready, the burners having been turned out for some time, the boat and contents are inserted. The burners are lighted from the forward end, gradually work backwards, and a slow current of oxygen about two bubbles per second having previously been turned on till the tube is full of oxygen. Regulate the temperature till the boat is at a dull red, and if the solution in the bulbs shows signs of running back to the furnace, increase the current of oxygen to three or four bubbles per second.

From the time of putting in the boat about fifty minutes will suffice

for a complete combustion. Turn off the oxygen and pass a current of air for ten minutes.

The potash bulbs and guard tube are now removed and weighed, and the carbon calculated as usual.

(*b*) **Graphitic Carbon.**—The iron is, by some, dissolved in HCl, by others in HNO_3, when the *graphitic* carbon remains as a residue. For pig-iron either method, with care, gives good results, but for steels containing graphite Blair recommends solution in nitric acid. (For this method consult Blair.)

Weigh out 5 gms. pig-iron borings. Dissolve in 50 c.cs. SE. HCl by aid of gentle heat. Boil for a few minutes. Dilute to 100 c.cs. (nearly). Filter through a Gooch crucible. Wash well with hot water and then with boiling E. KHO. (This dissolves any SiO_2.) Wash again with hot water to remove the KHO. Dry the crucible and contents.

Estimate the carbon as before by combustion, and calculate the percentage as usual.

(*c*) **Combined Carbon** (*by difference*).—The total carbon and the graphitic carbon being known, the combined carbon is obtained by subtracting the graphitic from the total carbon.

For direct methods of estimation consult the authorities mentioned.

(2) THE ESTIMATION OF SULPHUR IN IRON AND STEEL.

Considerable differences of opinion exist as to the best method of estimating sulphur in iron and steel. The *old* aqua regia solution and $BaCl_2$ precipitation method is admitted to be very inaccurate; but slow solution in HNO_3, with very little or no HCl present, followed by careful precipitation by $BaCl_2$ in presence of a *definite* excess of HCl, and with due care as to time and conditions of precipitation, and precautions against contamination of the precipitate by iron—with these and care good results are obtainable. Blair, on the other hand, recommends solution in HCl, the S being evolved as H_2S, which is absorbed in a solution (alkaline) of $Pb(NO_3)_2$ forming PbS, which is dissolved in $HCl + KClO_3$ and the S precipitated as $BaSO_4$. For further methods see Blair, Stillman, Auchy, Crobaugh, and Drown. Another method in common use is that of evolution of the S as H_2S, followed by absorption in cadmium chloride solution. The precipitated cadmium sulphide is dissolved in HCl and the S estimated by titration with an iodine solution, or more common still, the H_2S is absorbed in Br. water and then precipitated as $BaSO_4$, or is absorbed in NaOH and titrated with iodine; this latter being the favourite method. (See Blair.) The following method is here given:—

Oxidation by HNO_3 (the so-called **Aqua Regia method**).—Weigh out 5 gms. borings and transfer to a deep 200 c.c. beaker. Carefully add about 40 c.cs. 16E. HNO_3, in lots of about 10 c.cs. at a time, covering the beaker with a large watch glass and taking care that the action is not too violent. When the action apparently ceases, note if all the particles are dissolved (except any carbon). If not, heat on the sand bath, and add 3 or 4 drops of 16E. HCl, and warm till dissolved.

When solution is complete, add a little Na_2CO_3 to convert any H_2SO_4 into Na_2SO_4, which is non-volatile on evaporation.

Remove from the sand bath, and add 5 c.cs. of strong HCl in excess of that necessary to just dissolve any iron compounds precipitated by the Na_2CO_3. Filter off the SiO_2 and C. Wash well. Evaporate to dryness to render SiO_2 insoluble. Take up with HCl, and evaporate till Fe_2Cl_6 begins to crystallise out. Then add 5 c.cs. HCl, and filter if any residue is present. (If none is present, no SiO_2 was in solution, and the evaporation

could have been omitted.) Filter and wash carefully the precipitate in the Gooch, bringing the liquid and washings up to about 100 c.cs.

Heat to boiling. Add 10 c.cs. *saturated* solution of $BaCl_2$. Boil for 30 minutes. Allow to stand over-night. Filter through a Gooch. Wash with a little E. HCl, and then with water. Dry, ignite, and weigh as usual the $BaSO_4$, which should be white, and not contaminated with iron salts.

Calculate the percentage of S in the usual way. As some of the reagents used may contain sulphur, a blank must be run, using the same quantities as in the actual analysis, and any sulphur found deducted from the previous result.

(3) THE ESTIMATION OF SILICON.

The method here given is that of Drown, and is both rapid and exact. The iron is dissolved in HNO_3, followed by H_2SO_4, with evaporation to dryness. This is followed by solution, leaving the silicon in the residue as SiO_2.

Details.—Weigh out 2 gms. borings, and transfer to a platinum or porcelain dish. Add 30 c.cs. 8E. HNO_3. When the action apparently ceases, add 20 c.cs. 18E. H_2SO_4, and evaporate. (Blair recommends a gentle blast of hot air playing on the surface of the liquid. The air is heated by passing it through a small spiral of copper pipe heated over a bunsen. Evaporation is thus hastened and spirting prevented.) Continue the evaporation until copious fumes of SO_3 come off. Cool, and cautiously dilute with distilled water to 150 c.cs. Heat till all the $FeSO_4$ is dissolved. Filter, and wash first with a little E. HCl, and then with hot water. This filtration is best performed with a 7 cm. ashless filter paper (check the ash by igniting two or three of the papers). Dry; transfer to a platinum crucible; ignite as usual and weigh. To the crucible add 5 c.cs. strong H_2SO_4 and 5 c.cs. strong HF. Carefully evaporate to dryness, using a hot blast of air to hasten the evaporation. Ignite, and weigh again. Provided the H_2SO_4 and HF are pure, the difference in weight represents SiO_2. Check the H_2SO_4 and HF (particularly the latter) by evaporating a blank. Any residue found must be allowed for.

(4) THE ESTIMATION OF PHOSPHORUS.

Here, again, numerous methods are given by different authorities, the majority of them yielding accurate results when carefully followed out. The two methods most suited to technical analysis are the *volumetric reduction method* prepared by the sub-committee (Messrs Barba, Blair, Drown, Dudley, and Shimer) of the International Steel Standards Committee, U.S.A., and the *modified reduction method* as given by Messrs Dudley and Pease, *Jour. Anal. Appl. Chem.*, vii. 108. The former method is fully discussed in Blair's *Analysis of Iron*; the latter method is given here.

The iron is dissolved, and the P precipitated as phospho-molybdate of ammonium. This is dissolved, and by the action of Zn and H_2SO_4 the MoO_3 is reduced, and the reduced liquid is then titrated with $K_2Mn_2O_8$ (standard solution), and from the number of c.cs. used the P contents may be calculated.

Details.—Where much work is to be done, a shaking apparatus is necessary (see Chemical Supply Catalogues). The student, however, may perform the necessary shaking by hand. Before proceeding to the analysis, the reducing apparatus (a modification of the Jones reductor) must be prepared (see fig. 109).

At *a* is a finely perforated disc of stout platinum foil. Between *a* and *c* is about $\frac{3}{4}$ inch of clean white sand. *c* is another perforated platinum disc.

Above this disc the tube is filled with fine granulated amalgamated zinc, prepared thus:—Dissolve 5 gms. Hg in 25 c.cs. strong HNO_3, diluting with water and making the solution up to 1 litre. In this solution pour half a kilo of granulated zinc which passes a 20 but not a 30 sieve. Shake for one or two minutes. Pour off the solution. Wash and dry the zinc, which is now amalgamated. The funnel and flask are fitted to the apparatus as shown.

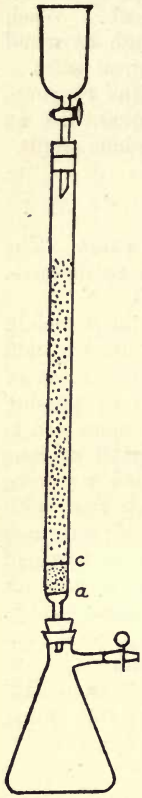

FIG. 109.

Prepare the following Reagents :—

(a) *The Strong Oxidising Solution of* $K_2Mn_2O_8$. 12 gms. *pure* $K_2Mn_2O_8$ in 1 litre water. Filter and bottle.

(b) *The Molybdate Solution.*—Dissolve 50 gms. MoO_3 in 200 c.cs. NH_4HO (S.G. ·96). Filter, and to the filtrate add 500 c.cs. HNO_3 (S.G. 1·2). Let stand at least 24 hours before using.

(c) *The Acid Ammonium Sulphate Solution.*—To 500 c.cs. distilled water add 27·5 c.cs. NH_4HO (S.G. 0·96), and then 24 c.cs. *pure* H_2SO_4 (S.G. 1·84), and dilute to 1000 c.cs.

(d) *The Standard* $K_2Mn_2O_8$ *Solution.*—Dissolve 2 gms. crystallised $K_2Mn_2O_8$ in 1000 c.cs. distilled water. Standardize the solution as follows: Weigh out 3 lots of from ·1 to ·3 gm. each of thoroughly cleaned iron wire, the iron contents of which are known. Transfer to 100 c.c. Erlenmeyer flask, and add to each 40 c.cs. 8E. H_2SO_4. When dissolved, boil 5 minutes; dilute to 150 c.cs., and pass through the reductor and wash, bringing the volume up to 200 c.cs., as directed in the analysis. Titrate each lot with the $K_2Mn_2O_8$. The results should agree for metallic iron to $\frac{1}{100}$ milligram. Make the required allowance for the impurities in the wire taken. Suppose 1 c.c. $K_2Mn_2O_8$ = ·0034923 gm. Fe, then multiply this value in Fe by the ratio of MoO_3 to Fe, namely, ·9076, and the product by ratio of the P present to the MoO_3, namely, ·019, we have

$$1 \text{ c.c. } K_2Mn_2O_8 = \cdot0000602 \text{ gm. P}$$

The Analysis.—Weigh out 1 gm. borings. Transfer to a 200 c.c. Erlenmeyer flask. Add 70 c.cs. 5E. HNO_3. When solution is complete, boil a minute, and add 10 c.cs. of the 'oxidising' solution of $K_2Mn_2O_8$. Boil till the pink colour disappears and MnO_2 separates out. Remove, and add gradually with stirring crystals of *pure* (phosphorus free) $FeSO_4$ till the contents clear up. Heat the solution to 80° C. (if As is present, to 35° C.). Add 75 c.cs. of the molybdate solution at a temperature of 27° C. Close the flask with a rubber stopper and shake for 5 minutes. Let stand for 5 minutes. Then filter through a 9 cm. filter, and wash with the acid amm. sulphate solution till a few drops of the washings give no colour with ammonium sulphide.

Dissolve the precipitate on the paper with 5 c.cs. NH_4HO (S.G. 0·90) and 25 c.cs. water, letting the solution run back into the original flask, thus dissolving any precipitate adhering to its sides. Wash till filtrate and washings amount to 150 c.cs. Add 10 c.cs. strong H_2SO_4 (S.G. 1·84), and dilute to 200 c.cs. The solution is now ready for reduction.

Pour 100 c.cs. warm $\frac{E.}{2}$ H_2SO_4 into the funnel. Connect the flask to the filter pump and open the clamp, so that the solution nearly, but not quite,

flows out of the funnel. Then to the funnel add the following blank—5 c.cs. NH_4HO (S.G. 0·90), 10 c.cs. H_2SO_4 (S.G. 1·84), and 50 c.cs. water, mixed together. Again open the clamp, so as to nearly run this mixture out of the funnel. Now add 200 c.cs. $\frac{E.}{2}H_2SO_4$ to the funnel, and nearly run through. Disconnect the flask, first closing the stopcock on the funnel. Titrate the contents of the flask with $K_2Mn_2O_8$. Generally about 0·1 c.cs. permanganate are thus consumed, and this quantity must be deducted from future readings.

Now transfer the solution to be reduced to the funnel. Attach a clean flask. Connect and start the filter pump. Open the stopcock and clamp, so as to nearly run through the solution. Wash out the flask that contained the solution with 100 c.cs. $\frac{E.}{2}$ H_2SO_4. Add this to the funnel, and treat as before. Finally, add and nearly run through another 100 c.cs. of the acid.

The reduced solution in the filter flask should now be bright green.

Remove as before and titrate with the permanganate solution. The green changes to pinkish brown, then pinkish yellow, then colourless, and finally a permanent pink is obtained (after standing one minute). From the reading obtained deduct the blank reading, and calculate the percentage of P present from the data given above.

Instead of this volumetric method, some chemists prefer to weigh directly the yellow phospho-molybdate precipitate. For details see Blair's *Analysis of Iron*, p. 108.

Note.—The student should, wherever possible, take advantage of references to special authorities. By this time he should be capable of consulting, comparing, and, to some extent, judiciously using such materials. No one *text-book* can give an anyway comprehensive treatment of 'Iron and Steels,' or, for that matter, of any one of the subjects treated of in this section; therefore such references as are given, together with current literature, must be carefully perused by the analyst who wishes to excel in technical work. The colorimetric determination of combined carbon by Eggertz's Method has been given; manganese may be determined somewhat similarly by Peter's Colorimetric Method, or by the Acetate Method (see Blair, etc.).

CHAPTER VIII.

THE PARTIAL ANALYSIS OF COPPER AND LEAD SLAGS.

For technical purposes it is rarely necessary to determine all the constituents present in a slag. The lead or copper smelter wishes to know the lead or copper contents of his slags; also their silver and gold contents (if any), and, as a rule, the silica, ferrous oxide, and lime present. Certain other constituents, such as sulphur, potassium, sodium, barium, magnesium, and aluminium, rarely require estimation. In certain cases the oxides of manganese and zinc are important constituents. It is difficult to lay down a scheme suitable to all cases and at the same time rapid in operation. The chemist must frequently construct his own scheme according to the number of substances to be determined. The methods here laid down, though only partial, are capable of contraction or expansion according as few or many determinations are to be made, and in making such alterations due precautions must be taken that any important steps in the treatment are not omitted when certain substances in a complete scheme are not determined. For instance, although **Cu**, **Pb**, **Bi**, etc. are not to be estimated, and the only determinations required are those of SiO_2, **FeO**, and **CaO**, the student must not omit the precipitation of the **Cu**, **Pb**, and **Bi** before proceeding to determine the **FeO**, etc. Whatever modification be adopted, the effect of any omissions or additions must be carefully considered, and where any doubt exists, the results should be checked by a complete analysis, aided by a thorough qualitative examination of all precipitates obtained.

The following estimations will here be considered in detail—

Pb, **Cu**, **Ag** and **Au**, SiO_2, **FeO**, and **CaO**.

To expedite matters, the samples of slag should be chilled when taken (consult text-books on Assaying), as in this state they are readily broken up by acid. The estimation of **Pb**, SiO_2, **FeO**, and **CaO** will be taken first, then that of the **Cu**, **Ag**, and **Au**.

Estimation of Pb and SiO_2.—Weigh out 2 gms. of the slag, finely ground in an agate mortar. Transfer to a 200 c.c. conical beaker. Add to the beaker, stirring continuously, 30 c.cs. 5E. **HCl**, 10 drops HNO_3, and 10 drops H_2SO_4. Evaporate to dryness. Take up with 30 c.cs. E. **HCl**. Filter (through paper) and wash well, keeping most of the precipitate in the beaker. The precipitate contains SiO_2, $PbSO_4$ (and $BaSO_4$). Reserve the solution. To the precipitate in the beaker add 10 c.cs. hot 5E. $NH_4C_2H_3O_2$. Boil for a few minutes and pass the solution through the filter paper into a clean beaker. Repeat the solution till no more **Pb** is dissolved (test). Wash the contents of the beaker on to the paper and wash well with hot water.

Dry, ignite, and weigh the precipitate. Note the weight. Test the precipitate for **Ba** (by flame coloration), and if present, fuse with about 5 times its bulk of Na_2CO_3,K_2CO_3 over the blast. Take up in hot water; boil and filter till all

soluble sulphates are washed through. The SiO_2 and $BaCO_3$ remain on the filter. Dissolve out the $BaCO_3$ with HCl. Filter, wash well, and precipitate the Ba as $BaSO_4$ in the usual manner. Deduct the $BaSO_4$ thus found from the weight of the precipitate previously found, and calculate the percentage of SiO_2.

Determine the lead in the acetate solution by Alexander's Molybdate method. (For a modified 'Fire' method consult Furman, p. 308.)

Estimation of FeO.—Pass H_2S through the filtrate from the SiO_2, $PbSO_4$, and $BaSO_4$. Filter. Boil off the H_2S. To the filtrate add NH_4HO till alkaline. Boil, filter, and wash once. Redissolve the precipitate in a little HCl. Reprecipitate as before. Filter, and combine the filtrates, reserving them for the lime estimation.

The Fe in the precipitate may be estimated by solution in H_2SO_4 and titration of part of the solution with $K_2Mn_2O_8$. Calculate from this the percentage of FeO.

Estimation of CaO.—Evaporate the combined filtrate from the iron to a bulk of about 100 c.cs. If not distinctly alkaline, make it so with NH_4HO. Precipitate the lime as usual with $(NH_4)_2C_2O_4$. Filter through a Gooch crucible. Wash well. Dissolve the precipitate, and estimate the CaO volumetrically by $K_2Mn_2O_8$ (standardised on a pure calcium salt).

Estimation of Silver and Gold.—This is best done by fire-assay. As only small quantities of these metals are present, 4 lots of 1 A.T. (30 gms.) each should be taken, and the buttons combined by scorification. In the Assaying Section of this book the student will find suitable charges.

The Estimation of Copper.—The following method, given by C. F. Shelby in the *N.Y. Eng. and Min. Journ.*, June 16, 1900, has been found by the author to give rapid and accurate results. The Cu is easily and completely separated in the presence of large amounts of SiO_2 and FeO, the complete estimation taking from 60 to 100 minutes.

Dissolve 5 gms. finely powdered slag in a 100 c.c. casserole or porcelain dish with cover, by moistening with a few c.cs. water 10 c.cs. strong HCl and 1 c.c. strong HNO_3. Heat till all the gelatinous SiO_2 is thoroughly dehydrated. Add 10 to 15 c.cs. strong HCl. Heat to boiling. Dilute and filter, washing first by decantation and then on the paper. To the filtrate, now about 150 c.cs. in bulk, gradually add a saturated solution of $Na_2S_2O_3,10H_2O$ till the yellow colour of the solution just disappears. Fe_2Cl_6 is now reduced to $FeCl_2$. In the solution place a coiled strip of sheet zinc, 2·5 c.m. × 5 c.m. Nascent H and S combine to form H_2S, and in about 30 to 60 seconds all the Cu is precipitated as Cu_2S. Filter and wash well after all the Zn has dissolved.

The Cu_2S may now be dissolved in HNO_3, and estimated volumetrically by KCN, or colorimetrically, or the Cu_2S may be dissolved, and the Cu estimated volumetrically by iodine and sodium thiosulphate.

Note.—The student is referred to the *Engineering and Mining Journal, N.Y.*, October 18th, 1902, and February 21st, 1903, for a letter and article by Thorn Smith, giving details of results of slag analyses and suggestions for improvement of methods. He cannot do better than read these references and benefit by them; they show what care is necessary in obtaining accurate results, and will do much to further the degree of accuracy obtainable in such work, and, at the same time, they clearly lay down the standard of excellence at which the student should aim.

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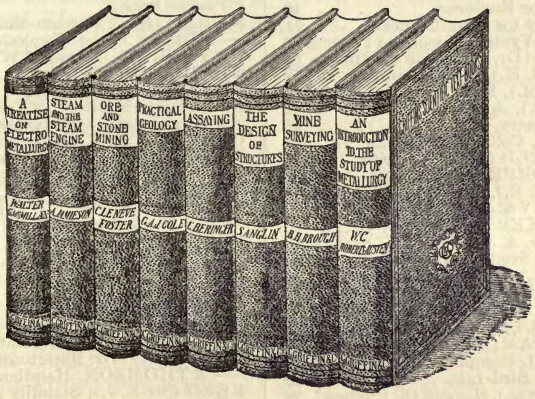

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